

# Crystallization Processes

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## GLOSSARY

**Crystallizer** The vessel or process unit in which crystallization occurs.

**Growth** The increase in crystal size due to deposition of solute on crystal surfaces.

**Magma** The mixture of crystals and mother liquor in the crystallizer.

**Mode of crystallization** The means by which a thermodynamic driving force for crystallization is created.

**Mother liquor** The liquid solution from which crystals are formed.

**MSMPR crystallizer** A vessel operating in a continuous manner in which crystallization occurs and whose contents are perfectly mixed. As a result of perfect mixing, all variables descriptive of the mother liquor and crystals are constant throughout the vessel and are identical to corresponding variables in the product stream leaving the vessel.

**Nucleation** The formation of new crystals.

**Primary nucleation** The formation of crystals by mechanisms that do not involve existing crystals of the crys-

tallizing species; includes both homogeneous and heterogeneous nucleation mechanisms.

**Secondary nucleation** The formation of crystals through mechanisms involving existing crystals of the crystallizing species.

**Solubility** The equilibrium solute concentration. The dimensions in which solubility is expressed include, but are not limited to, mass or mole fraction, mass or mole ratio of solute to solvent, and mass or moles of solute per unit volume of solvent or solution.

**Supersaturation** The difference between existing and equilibrium conditions; the quantity represents the driving force for crystal nucleation and growth.

**CRYSTALLIZATION PROCESSES** addressed in this discussion are used in the chemical, petrochemical, pharmaceutical, food, metals, agricultural, electronics, and other industries. Moreover, the principles of crystallization are important in all circumstances in which a solid crystalline phase is produced from a fluid, even when the solid is not a product of the process. Much has been done

in recent years to improve the understanding of crystallization, and a large portion of the research on the topic has dealt with mechanisms of nucleation and growth. Especially important has been elucidation of the effects of process variables on the rates at which these phenomena occur. Additionally, extensive progress has been achieved in modeling both steady-state and dynamic behavior of crystallization systems of industrial importance. The primary elements of the discussion that follows are the principles that influence yield, morphology, and size distribution of crystalline products.

## I. OBJECTIVES OF CRYSTALLIZATION PROCESSES

Several examples of objectives that may be satisfied in crystallization processes are given in the following discussion. Soda ash (sodium carbonate) is recovered from brine by contacting the brine with carbon dioxide that reacts with sodium carbonate to form sodium bicarbonate. Sodium bicarbonate, which has a lower solubility than sodium carbonate, crystallizes as it is formed. The primary objective of the crystallizers used in this process is separation of a high percentage of sodium bicarbonate from the brine in a form that facilitates segregation of the crystals from the mother liquor. The economics of crystal separation from the mother liquor are affected primarily by the variables that control the flow of liquid through the cake of crystals formed on a filter or in a centrifuge. For example, the flow rate of liquid through a filter cake depends on the available pressure drop across a filter, liquid viscosity, and the size distribution of crystals collected on the filter. With a fixed available pressure drop and defined liquid properties, the crystal size distribution controls filter throughput and, concomitantly, the production rate from the process.

Crystallization can be used to remove solvent from a liquid solution. For example, concentration of fruit juice requires the separation of solvent (water) from the natural juice. The common procedure is evaporation, but the derived juices may lose flavor components or undergo thermal degradation during the evaporative process. In freeze concentration, the solvent is crystallized (frozen) in relatively pure form to leave behind a solution with a higher solute concentration than the original mixture. Significant advantages in product taste have been observed in the application of this process to concentrations of various types of fruit juice.

The elimination of small amounts of an impurity from a product species may be an objective of crystallization. In such instances, a multistep crystallization–redissolution–recrystallization process may be required to produce a

product that meets purity specifications. For example, in the manufacture of the amino acid L-isoleucine, the product is first recovered in acid form, redissolved, neutralized, and then recrystallized in order to exclude the impurity L-leucine and other amino acids from the product.

A simple change in physical properties also can be achieved by crystallization. In the process of making soda ash, referred to earlier, the sodium bicarbonate crystals are subjected to heat that causes the release of carbon dioxide and produces low-density sodium carbonate crystals. The density of these crystals is incompatible with their use in glass manufacture, but a more acceptable crystal can be obtained by contacting the sodium carbonate crystals with water to form crystalline sodium carbonate monohydrate. Drying the resulting crystals removes the water of hydration and produces a dense product that is acceptable for glass manufacture.

Separation of a chemical species from a mixture of similar compounds can be achieved by crystallization. The mode of crystallization may fall in the realm of what is known as melt crystallization. In such processes, the mother liquor largely is comprised of the melt of the crystallizing species, and, subsequent to its crystallization, crystals formed from the mother liquor are remelted to produce the product from the crystallizer. *Para(p)*-xylene can be crystallized from a mixture that includes *ortho* and *meta* isomers in a vertical column that causes crystals and mother liquor to move countercurrently. Heat is added at the bottom of the column to melt the *p*-xylene crystals; a portion of the melt is removed from the crystallizer as product and the remainder flows up the column to contact the downward-flowing crystals. Effluent mother liquor, consisting almost entirely of the *ortho* and *meta* isomers of xylene, is removed from the top of the column.

Production of a consumer product in a form suitable for use and acceptable to the consumer also may be an objective of a crystallization process. For example, sucrose (sugar) can be crystallized in various forms. However, different cultures are accustomed to using sugar that has a particular appearance and, unless the commodity has that appearance, the consumer may consider the sugar to be unacceptable.

In all these processes, there are common needs: to form crystals, to cause them to grow, and to separate the crystals from the residual liquid. While conceptually simple, the operation of a process that utilizes crystallization can be very complex. The reasons for such complexity involve the interaction of the common needs and process requirements on product yield, purity, and, uniquely, crystal morphology and size distribution. In the following discussion, the interactions will be discussed and general principles affecting crystallizer operation will be outlined. More

extensive discussion of the subject matter can be found in the bibliography at the end of the chapter.

## II. EQUILIBRIUM AND MASS AND ENERGY BALANCES

### A. Solid–Liquid Equilibrium

The solubility of a chemical species in a solvent refers to the amount of solute that can be dissolved at constant temperature, pressure, and solvent composition (including the presence of other solutes). In other words, it is the concentration of the solute in the solvent at equilibrium.

As with all multiphase systems, the Gibbs phase rule provides a useful tool for determining the number of intensive variables (ones that do not depend on system mass) that can be fixed independently:

$$N_{DF} = N_c - N_p + 2 \quad (1)$$

$N_{DF}$  is the number of degrees of freedom,  $N_c$  is the number of components, and  $N_p$  is the number of phases in the system. The number of degrees of freedom represents the number of independent variables that must be specified in order to fix the condition of the system. For example, the Gibbs phase rule specifies that a two-component, two-phase system has two degrees of freedom. If temperature and pressure are selected as the specified variables, then all other intensive variables—in particular, the composition of each of the two phases—are fixed, and solubility diagrams of the type shown for a hypothetical mixture of R and S in Fig. 1 can be constructed.

Several features of the hypothetical system described in Fig. 1 illustrate the selection of crystallizer operating

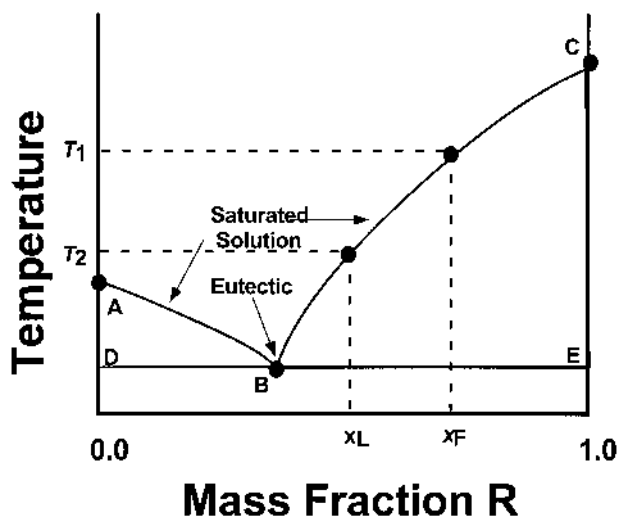


FIGURE 1 Hypothetical solubility diagram of eutectic-forming system.

conditions and the limitations placed on the operation by the system properties. The curves AB and BC represent solution compositions that are in equilibrium with solids whose compositions are given by the lines AD and CE, respectively. If AD and CE are vertical and coincident with the left and right extremes, the crystals are pure S and R, respectively. Crystallization from any solution whose equilibrium composition is to the left of a vertical line through point B will produce crystals of pure S, while solutions with an equilibrium composition to the right of the line will produce crystals of pure R. A solution whose composition falls on the line through B will produce a mixture of crystals of R and S.

Now suppose a saturated solution at temperature  $T_1$  is fed to a crystallizer operating at temperature  $T_2$ . Since it is saturated, the feed has a mole fraction of R equal to  $x_F$ . The maximum production rate of crystals occurs when the solution leaving the crystallizer is saturated, meaning that the crystal production rate,  $m_{\text{prod}}$ , depends on the value of  $T_2$ :

$$m_{\text{prod}} = m_F x_F - m_L x_L \quad (2)$$

where  $m_F$  is the feed rate to the crystallizer and  $m_L$  is the solution flow rate leaving the crystallizer. Note that the lower limit on  $T_2$  is given by the eutectic point, and that attempts to operate the crystallizer at a temperature other than the eutectic value will result in a mixture of crystals of R and S.

When certain solutes crystallize from aqueous solutions, the crystals are hydrated salts, which means that the crystals contain water and solute in a specific stoichiometric ratio. The water in such instances is referred to as *water of hydration*, and the number of water molecules associated with each solute molecule may vary with the crystallization temperature.

Potassium sulfate provides an example of such behavior. When it crystallizes from an aqueous solution above 40°C, the crystals are anhydrous  $\text{K}_2\text{SO}_4$ , while below 40°C each molecule of  $\text{K}_2\text{SO}_4$  that crystallizes has 10 molecules of water associated with it. The hydrated salt,  $\text{K}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}(\text{s})$ , is called potassium sulfate decahydrate. Another solute that forms hydrated salts is magnesium sulfate, which can incorporate differing amounts of water depending upon the temperature at which crystallization occurs (see Table I).

The solubility diagrams of several species are shown in Fig. 2, and these illustrate the importance of solubility behavior in the selection of the mode of crystallization. For example, consider the differences between potassium nitrate and sodium chloride: The solubility of potassium nitrate is strongly influenced by the system temperature, whereas the opposite is true for sodium chloride. As a consequence, (1) a high yield of potassium nitrate crystals can be obtained by cooling a saturated feed solution,

**TABLE I** Water of Hydration for  $\text{MgSO}_4$ 

Form	Name	wt% $\text{MgSO}_4$	Conditions
$\text{MgSO}_4$	Anhydrous magnesium sulfate	0.0	$>100^\circ\text{C}$
$\text{MgSO}_4 \cdot \text{H}_2\text{O}$	Magnesium sulfate monohydrate	87.0	67 to $100^\circ\text{C}$
$\text{MgSO}_4 \cdot 6\text{H}_2\text{O}$	Magnesium sulfate hexahydrate	52.7	48 to $67^\circ\text{C}$
$\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$	Magnesium sulfate heptahydrate	48.8	2 to $48^\circ\text{C}$
$\text{MgSO}_4 \cdot 12\text{H}_2\text{O}$	Magnesium sulfate dodecahydrate	35.8	$-4$ to $2^\circ\text{C}$

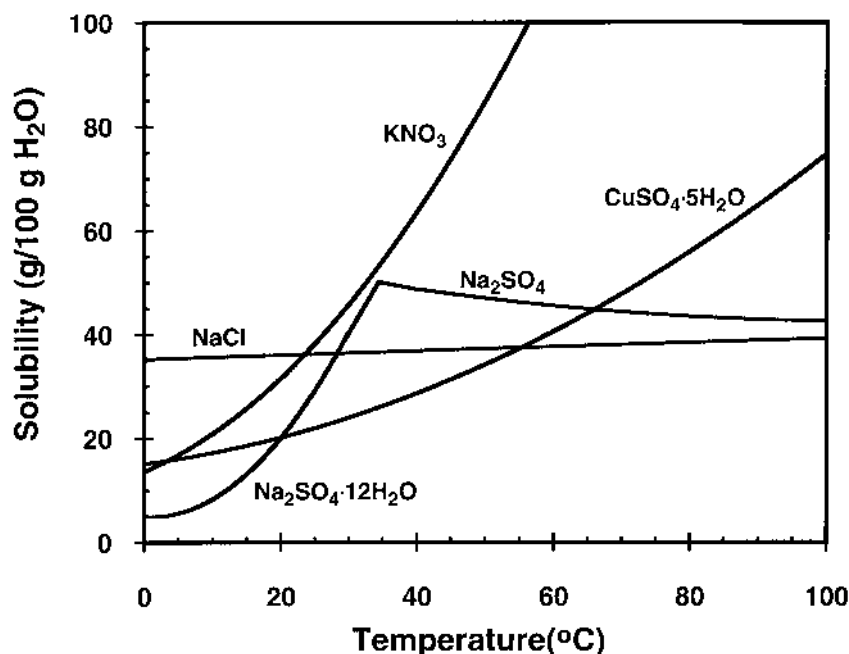
but (2) cooling a saturated sodium chloride solution accomplishes little crystallization, and vaporization of water is required to increase the yield.

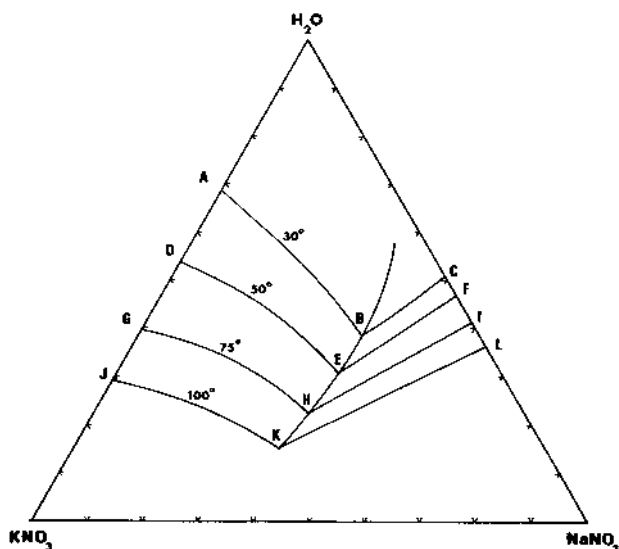
The effect of water of hydration on solubility can be seen in Fig. 2. Note, for example, that sodium sulfate has two forms in the temperature range of the solubility diagram: sodium sulfate decahydrate ( $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ ), which is known as Glauber's salt, and anhydrous sodium sulfate. Since a transition from Glauber's salt to anhydrous sodium sulfate occurs at approximately  $34^\circ\text{C}$ , crystals recovered from a crystallizer operating above about  $34^\circ\text{C}$  will be anhydrous, but those from a crystallizer operating below this temperature will contain 10 waters of hydration. Also observe the effect of water of hydration on solubility characteristics; clearly, cooling crystallization could be used to recover significant yields of Glauber's salt but evaporative crystallization would be required to obtain high yields of the anhydrous salt.

Mixtures of multiple solutes in a single solvent are encountered in a number of processes—for example, in the recovery of various chemicals from ores or brines. Express-

sion of the complex solubility behavior in such systems by graphical means usually is limited to systems of two solutes. The interaction of added solutes on solubility is illustrated by the plot of equilibrium behavior for potassium nitrate–sodium nitrate–water in Fig. 3. As before, the curves in the diagram trace solution compositions that are in equilibrium with solid solutes. Points A, D, G, and J are based on the solubilities of pure potassium nitrate, while points C, F, I, and L are based on solubilities of pure sodium nitrate. Curves AB, DE, GH, and JK represent compositions of solutions in equilibrium with solid potassium nitrate at 30, 50, 70, and  $100^\circ\text{C}$ , respectively. Curves BC, EF, HI, and KL represent compositions of solutions in equilibrium with solid sodium nitrate. Should the solution condition, including temperature, correspond to points B, E, H, K or any condition on the curve connecting these points, crystals of both solutes would be formed by cooling.

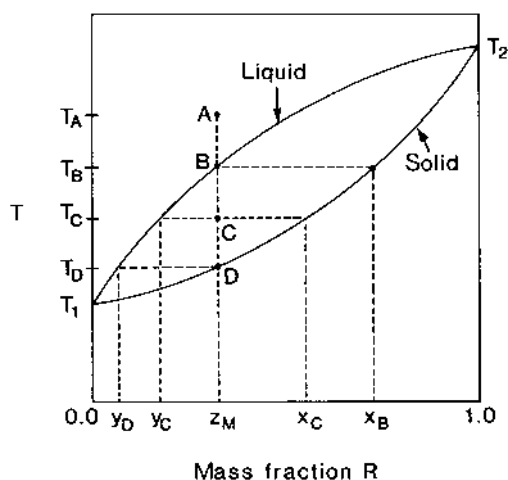
A second type of solubility behavior is exhibited by mixtures that form solid solutions. Consider, for example, a hypothetical system containing R and S whose

**FIGURE 2** Solubility diagram for several common substances.



**FIGURE 3** Solubility diagram of  $\text{KNO}_3$  and  $\text{NaNO}_3$  mixtures in water.

equilibrium behavior is described in Fig. 4. The phase envelope is drawn based on the compositions of coexisting liquid and solid phases at equilibrium. The pure component R has a melting point at pressure  $P$  equal to  $T_2$  while the melting point of pure S is  $T_1$ . The system behavior can best be described by the following example: Consider a mixture of R and S at temperature  $T_A$  and having a mass fraction of R equal to  $z_M$ . From the phase diagram, the mixture is a liquid. As the liquid is cooled, a solid phase forms when the temperature reaches  $T_B$  and the system is allowed to come to equilibrium; the solid-phase composition corresponds to a mass fraction of R equal to  $x_B$ . On cooling the liquid further, the ratio of solid to liquid in-



**FIGURE 4** Hypothetical solubility diagram of mixture without a eutectic at constant pressure:  $x$ , solid;  $y$ , liquid;  $z$ , combined.

creases and at  $T_C$  the mass fraction of R in the liquid is  $y_C$  and in the solid it is  $x_C$ . At  $T_D$  the liquid phase disappears, leaving a solid with a mass fraction of R equal to  $z_M$ .

Systems that exhibit behavior of the type illustrated in Fig. 4 cannot be purified in a single crystallization stage. They represent situations in which multiple stages or continuous-contacting devices may be useful. The principles of such operations are analogous to those of other countercurrent contacting operations—for example, distillation, absorption, and extraction.

Variables other than temperature and the presence of other solutes can influence solubility. For example, the effect of a nonsolvent on solubility sometimes is used to bring about recovery of a solute. Figure 5 shows the solubility of L-serine in aqueous solutions containing varying amounts of methanol. Note that increasing methanol content reduces the solubility by more than an order of magnitude, and this characteristic can be used to obtain a high yield in the recovery of L-serine.

There is increasing interest in the crystallization of solutes from supercritical-fluid solvents. In such instances, solubilities often are correlated by an equation of state. Such concepts are beyond the scope of the current discussion but are presented elsewhere in the encyclopedia.

Although this discussion provides insight to the types of solubility behavior that can be exhibited by various systems, it is by no means a complete survey of the topic. Extensive solubility data and descriptions of more complex equilibrium behavior can be found in the literature. Published data usually consist of the influence of temperature on the solubility of a pure solute in a pure solvent; seldom are effects of other solutes, co-solvents, or pH considered. As a consequence, solubility data on a system of interest should be measured experimentally, and the solutions used in the experiments should be as similar as possible to those expected in the process. Even if a crystallizer has been designed and the process is operational, obtaining solubility data using mother liquor drawn from the crystallizer or a product stream would be wise. Moreover, the solubility should be checked periodically to see if it has changed due to changes in the upstream operations or raw materials.

There have been advances in the techniques by which solid-liquid equilibria can be correlated and, in some cases, predicted. These are described in references on phase-equilibrium thermodynamics.

## B. Mass and Energy Balances

Illustrating the formulation of mass and energy balances is simplified by restricting the analysis to systems whose crystal growth kinetics are sufficiently fast to utilize essentially all of the supersaturation provided by the crystallizer; in other words, the product solution

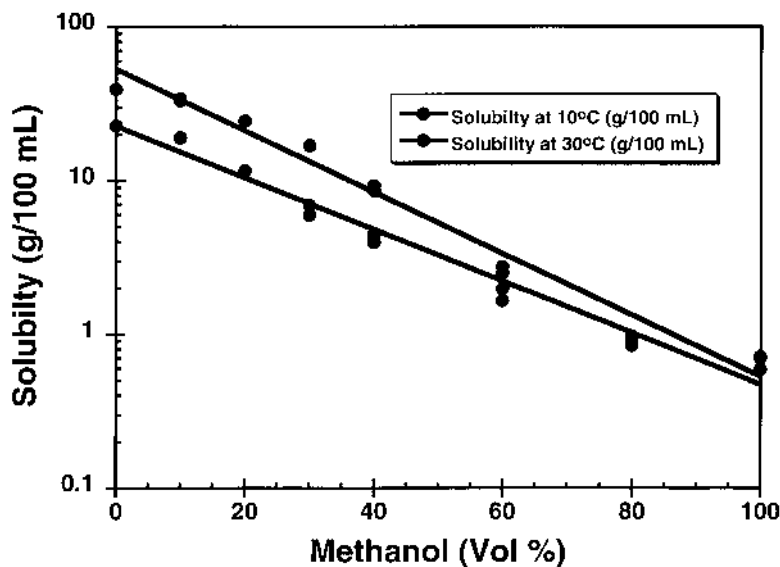


FIGURE 5 Effect of methanol on solubility of L-serine.

is assumed to be saturated. Under such conditions (referred to in the crystallization literature as Class II or fast-growth behavior), the solute concentration in the mother liquor can be assigned a value corresponding to saturation. Should the supersaturation in the mother liquor be so great as to affect the solute balance, the operation is said to follow Class I or slow-growth behavior. In Class I behavior, the operating conditions affect the rate at which solute is crystallized, and an expression coupling the rate of growth to a solute balance must be used to describe the system. Such treatment will be considered beyond the scope of this discussion.

The solution of mass and energy balances requires solubility and enthalpy data on the system of interest. Various methods of presenting solubility data were given earlier, and the use of solubilities to estimate crystal production rates from a cooling crystallizer was demonstrated by the discussion of Eq. (2). Subsequent to determining the yield, the rate at which heat must be removed from the crystallizer can be calculated from an energy balance:

$$m_C \hat{H}_C + m_L \hat{H}_L - m_F \hat{H}_F = Q \quad (3)$$

where  $m_F$ ,  $m_C$ , and  $m_L$  are feed rate, crystal production rate, and mother liquor flow rate, respectively;  $\hat{H}$  is specific enthalpy of the stream corresponding to the subscript; and  $Q$  is the required rate of heat transfer to the crystallizer. As  $m_F$ ,  $m_C$ , and  $m_L$  are known or can be calculated from a simple mass balance, determination of  $Q$  requires estimation of specific enthalpies. These are most conveniently obtained from enthalpy-composition diagrams, which are available in the general literature for a number of substances.

If specific enthalpies are unavailable, they can be estimated based on defined reference states for both solute and solvent. Often the most convenient reference states are crystalline solute and pure solvent at an arbitrarily chosen reference temperature. The reference temperature selected usually corresponds to that at which the heat of crystallization,  $\Delta \hat{H}_c$ , of the solute is known. (The heat of crystallization is approximately equal to the negative of the heat of solution.) For example, if the heat of crystallization is known at  $T_{\text{ref}}$ , then reasonable reference conditions would be the solute as a solid and the solvent as a liquid, both at  $T_{\text{ref}}$ . The specific enthalpies could be estimated then as:

$$\hat{H}_F = x_F \Delta \hat{H}_c + C_{pF}(T - T_{\text{ref}}) \quad (4)$$

$$\hat{H}_C = C_{pC}(T - T_{\text{ref}}) \quad (5)$$

$$\hat{H}_L = x_L \Delta \hat{H}_c + C_{pL}(T - T_{\text{ref}}) \quad (6)$$

where  $x_F$  and  $x_L$  are the mass fractions of solute in the feed and mother liquor, respectively. All that is required now to determine the required rate of heat transfer is the indicated heat capacities, which can be estimated based on system composition or measured experimentally.

Now suppose some of the solvent is evaporated in the crystallizer. Independent balances can be written on total and solute masses:

$$m_F = m_V + m_L + m_C \quad (7)$$

$$x_F m_F = x_L m_L + x_C m_C \quad (8)$$

Assuming that the streams leaving the crystallizer are in equilibrium, there is a relationship between the temperature (or pressure) at which the operation is conducted

and  $x_L$  and  $x_C$ . In addition, an energy balance must be satisfied:

$$m_F \hat{H}_F + Q = m_V \hat{H}_V + m_L \hat{H}_L + m_C \hat{H}_C \quad (9)$$

The specific enthalpies in the above equation can be determined as described earlier, provided the temperatures of the product streams are known. Evaporative cooling crystallizers (described more completely in Section V) operate at reduced pressure and may be considered adiabatic. In such circumstances, Eq. (9) is modified by setting  $Q = 0$ . As with many problems involving equilibrium relationships and mass and energy balances, trial-and-error computations are often involved in solving Eqs. (7) through (9).

### III. NUCLEATION AND GROWTH KINETICS

The kinetics of crystallization have constituent phenomena in crystal nucleation and growth. The rates at which these occur are dependent on driving forces (usually expressed as supersaturation), physical properties, and process variables, but relationships between these quantities and crystallization kinetics often are difficult to express quantitatively. As a result, empirical or qualitative links between a process variable and crystallization kinetics are useful in providing guidance in crystallizer design and operation and in developing strategies for altering the properties of crystalline products.

Nucleation and growth can occur simultaneously in a supersaturated environment, and the relative rates at which these occur are primary determinants of the characteristics of the crystal size distribution; one way of influencing product size distributions is through the control of variables such as supersaturation, temperature, and mixing characteristics. Obviously, those factors that increase nucleation rates relative to growth rates lead to a crystal size distribution consisting of smaller crystals. In the discussion that follows, an emphasis will be given to the general effects of process variables on nucleation and growth, but the present understanding of these phenomena does not allow quantitative *a priori* prediction of the rates at which they occur.

#### A. Supersaturation

Supersaturation is the thermodynamic driving force for both crystal nucleation and growth; and therefore, it is the key variable in setting the mechanisms and rates by which these processes occur. It is defined rigorously as the deviation of the system from thermodynamic equilibrium and is quantified in terms of chemical potential,

$$\Delta\mu_i = \mu_i - \mu_i^* = RT \ln \frac{a_i}{a_i^*} \quad (10)$$

where  $\mu_i$  is the chemical potential of solute  $i$  at the existing conditions of the system,  $\mu_i^*$  is the chemical potential of the solute equilibrated at the system conditions, and  $a_i$  and  $a_i^*$  are activities of the solute at the system conditions and at equilibrium, respectively. Less abstract definitions involving measurable system quantities are often used to approximate supersaturation; these involve either temperature or concentration (mass or moles of solute per unit volume or mass of solution or solvent) or mass or mole fraction of solute. Recommendations have been made that it is best to express concentration in terms of moles of solute per unit mass of solvent. For systems that form hydrates, the solute should include the water of hydration, and that water should be deducted from the mass of solvent.

Consider, for example, a system at temperature  $T$  with a solute concentration  $C$ , and define the equilibrium temperature of a solution having a concentration  $C$  as  $T^*$  and the equilibrium concentration of a solution at  $T$  as  $C^*$ . These quantities may be used to define the following approximate expressions of supersaturation:

1. The difference between the solute concentration and the concentration at equilibrium,  $\Delta C_i = C_i - C_i^*$
2. For a solute whose solubility in a solvent increases with temperature, the difference between the temperature at equilibrium and the system temperature,  $\Delta T = T^* - T$
3. the supersaturation ratio, which is the ratio of the solute concentration and the equilibrium concentration,  $S_i = C_i / C_i^*$
4. The ratio of the difference between the solute concentration and the equilibrium concentration to the equilibrium concentration,  $\sigma_i = (C_i - C_i^*) / C_i^* = S_i - 1$ , which is known as relative supersaturation.

Any of the above definitions of supersaturation can be used over a moderate range of system conditions, but as outlined in the following paragraph, the only rigorous expression is given by Eq. (10).

The definitions of supersaturation ratio and relative supersaturation can be extended to any of the other variables used in the definition of supersaturation. For example, defining  $S_{a_i} = a_i / a_i^*$  gives:

$$\frac{\Delta\mu_i}{RT} = \ln S_{a_i} = \ln \frac{\gamma_i C_i}{\gamma_i^* C_i^*} \quad (11)$$

Therefore, for ideal solutions or for  $\gamma_i \approx \gamma_i^*$ ,

$$\frac{\Delta\mu_i}{RT} \approx \ln \frac{C_i}{C_i^*} = \ln S_i \quad (12)$$

Furthermore, for low supersaturations (say,  $S_i < 1.1$ ),

$$\frac{\Delta\mu_i}{RT} \approx S_i - 1 = \sigma_i \quad (13)$$

The simplicity of Eq. (13) results in the use of relative supersaturation in most empirical expressions for nucleation and growth kinetics. While beguilingly simple, and correct in limiting cases, great care should be taken in extending such expressions beyond conditions for which the correlations were developed.

For ionic solutes,  $a_i = a_{\pm}^{\nu}$ , which leads to  $S_{a_i} = (a_{\pm}/a_{\pm}^*)^{\nu}$  and

$$\frac{\Delta\mu_i}{RT} = \nu \ln S_{a_i} = \nu \ln \frac{\gamma_{i\pm} C_i}{\gamma_{i\pm}^* C_i^*} \quad (14)$$

Again, for  $\gamma_{i\pm} \approx \gamma_{i\pm}^*$ ,

$$\frac{\Delta\mu_i}{RT} \approx \nu \ln \frac{C_i}{C_i^*} = \nu \ln S_i \quad (15)$$

## B. Primary Nucleation

The term *primary nucleation* is used to describe both homogeneous and heterogeneous nucleation mechanisms in which solute crystals play no role in the formation of new crystals. Primary nucleation mechanisms involve the formation of crystals through a process in which constituent crystal units are stochastically combined. Both homogeneous and heterogeneous nucleation require relatively high supersaturations, and they exhibit a high-order dependence on supersaturation. As will be shown shortly, the high-order dependence has a profound influence on the character of crystallization processes in which primary nucleation is the dominant means of crystal formation.

The classical theoretical treatment of primary nucleation that produces a spherical nucleus results in the expression:

$$\begin{aligned} B^{\circ} &= A \exp\left(-\frac{16\pi\epsilon_{\text{surf}}^3 v^2}{3k^3 T^3 [\ln(\sigma + 1)]^2}\right) \\ &\approx^{\sigma < 0.1} A \exp\left(-\frac{16\pi\epsilon_{\text{surf}}^3 v^2}{3k^3 T^3 \sigma^2}\right) \end{aligned} \quad (16)$$

where  $k$  is the Boltzmann constant,  $\epsilon_{\text{surf}}$  is the interfacial surface energy per unit area,  $v$  is molar volume of the crystallized solute, and  $A$  is a constant.

The theory shows that the most important variables affecting the rates at which primary nucleation occur are interfacial energy  $\epsilon_{\text{surf}}$ , temperature  $T$ , and supersaturation  $\sigma$ . The high-order dependence of nucleation rate on these three variables, especially supersaturation, is important because, as shown by an examination of Eq. (16), a small change in any of the three variables could produce an enormous change in nucleation rate. Such behavior gives rise to the often observed phenomenon of having a clear

liquor transformed to a slurry of very fine crystals with only a slight increase in supersaturation, for example by decreasing the solution temperature.

The effect of exogenous solid matter (as in heterogeneous nucleation) in the supersaturated solution is equivalent to that of a catalyst in a reactive mixture. Namely, it is to reduce the energy barrier to the formation of a new phase. In effect, the solid matter reduces the interfacial energy  $\epsilon_{\text{surf}}$  by what may amount to several orders of magnitude.

The classical nucleation theory embodied in Eq. (16) has a number of assumptions and physical properties that cannot be estimated accurately. Accordingly, empirical power-law relationships involving the concept of a metastable limit have been used to model primary nucleation kinetics:

$$B^{\circ} = k_N \sigma_{\text{max}}^n \quad (17)$$

where  $k_N$  and  $n$  are parameters fit to data and  $\sigma_{\text{max}}$  is the supersaturation at which nuclei are observed when the system is subjected to a specific protocol. Although Eq. (17) is based on empiricism, it is consistent with the more fundamental Eq. (16).

## C. Secondary Nucleation

Secondary nucleation is the formation of new crystals through mechanisms involving existing solute crystals; in other words, crystals of the solute *must* be present for secondary nucleation to occur. Several features of secondary nucleation make it important in the operation of industrial crystallizers: First, continuous crystallizers and seeded batch crystallizers have crystals in the magma that can participate in secondary nucleation mechanisms. Second, the requirements for the mechanisms of secondary nucleation to be operative are fulfilled easily in most industrial crystallizers. Finally, many crystallizers are operated in a low supersaturation regime so as to maximize yield, and at such supersaturations the growth of crystals is more likely to produce desired morphologies and high purity; these low supersaturations can support secondary nucleation but not primary nucleation.

### 1. Mechanisms

Secondary nucleation can occur through several mechanisms, including initial breeding, contact nucleation (also known as collision breeding), and shear breeding. Although a universal expression for the kinetics of secondary nucleation does not exist, a working relationship often can be obtained by correlating operating data from a crystallizer with a semi-empirical expression. Guidance as to the



form of the expression and the variables that it should include can be obtained by understanding the various mechanisms of secondary nucleation.

Initial breeding results from immersion of seed crystals in a supersaturated solution, and it is thought to be caused by dislodging extremely small crystals that were formed on the surface of larger crystals during drying. Although this mechanism is unimportant in continuous and unseeded batch crystallization, it can have a significant impact on the operation of seeded batch crystallizers. The number of crystals formed by initial breeding, has been found to be proportional to the surface area of crystals used to seed a batch crystallizer. Characteristics of the resulting distribution are affected strongly by the growth kinetics of nuclei resulting from initial breeding, and the phenomenon of growth-rate dispersion (which will be discussed later) can lead to erroneous conclusions regarding the nucleation kinetics.

Shear breeding results when supersaturated solution flows by a crystal surface and carries with it crystal precursors believed formed in the region of the growing crystal surface. High supersaturation is required for shear breeding to produce significant numbers of nuclei.

Contact nucleation in industrial processes results from collisions of crystals with the impeller used for circulation of the magma or with other crystallizer internals such as baffles, pipe and crystallizer walls, and even other crystals. Careful experimental studies have shown that the number of crystals produced by collisions between crystals and these objects depends upon the collision energy, supersaturation at impact, supersaturation at which crystals mature, material of the impacting object, area and angle of impact, and system temperature. The collision energy for contact nucleation is small and does not necessarily result in the macroscopic degradation or attrition of the contacted crystal.

Nucleation from collisions between crystals in the circulating magma and the rotor in a circulation pump or an agitator usually dominate nucleation resulting from other collisions. The operating variables in systems of this type can be manipulated to some extent, thereby modifying nucleation rates and the concomitant crystal size distribution. For example, internal classification can be used to keep larger crystals away from energetic collisions with an impeller, but doing so may create other problems with stability of the crystal size distribution. The rotational speed of an impeller can be changed if there are appropriate controls on the pump or agitator. Caution must be exercised, however, for a reduction in circulation velocity can reduce heat-transfer coefficients and increase fouling (encrustation) on heat-transfer surfaces. Moreover, the crystals in the magma must be kept suspended or crystal morphology and growth rates could be affected adversely. Impact

energy may have a high-order dependence on rotational speed and, if that is the case, modest changes in this variable could alter nucleation rates substantially. The fraction of the impact energy transmitted from an impeller to the crystal can be manipulated by changing the material of construction of the impeller. The influence of using soft materials to coat impellers or crystallizer internals may vary from one crystalline system to another; those systems in which the crystal face is soft may be more susceptible to nucleation rate changes than those crystalline systems where the face is hard.

Supersaturation has been observed to affect contact nucleation, but the mechanism by which this occurs is not clear. There are data that infer a direct relationship between contact nucleation and crystal growth; these data showed that the number of nuclei produced by an impact was proportional to the linear growth rate of the impacted face. This could indicate that the effect of supersaturation is to alter growth rates and, concomitantly, the characteristics of the impacted crystal faces; alternatively, what appears to be a mechanistic relationship actually could be a result of both nucleation and growth depending upon supersaturation.

Another theory that could account for the effect of supersaturation on contact nucleation is based on the view that nuclei formed cover a range of sizes that includes the critical nucleus. Since only the nuclei larger than the critical nucleus are stable, the relationship of the size of the critical nucleus to supersaturation reflects the dependence of contact nucleation on supersaturation. This concept, which has been referred to as a survival theory, seems to have been refuted by measurements of the sizes of crystals formed by collisions. These sizes are much larger than the critical nucleus, and the survival theory would have little influence on the number of nuclei that survive.

Evidence of the formation of polymolecular clusters in supersaturated solutions may provide a mechanistic interpretation of the effect of supersaturation on contact nucleation kinetics. These clusters may participate in nucleation, although the mechanism by which this would occur is not clear. One model that has been proposed, however, calls for the formation of a semi-ordered region consisting of molecular clusters awaiting incorporation into the crystal lattice. Collisions or fluid shear of the region containing high cluster concentrations could then result in these clusters serving as secondary nuclei. In such a model, the variables that influence formation and diffusion of the clusters also influence crystal growth rates and nucleation.

## 2. Kinetic Expressions

Irrespective of the actual mechanisms by which contact nucleation occurs, empirical power-law expressions

provide a useful means of correlating nucleation kinetics and using the resulting correlations in process analysis and control. The correlations generally take the form:

$$B^\circ = k_N \sigma^i M_T^j N^k \quad (18)$$

where  $k_N$ ,  $i$ ,  $j$ ,  $k$  are positive parameters obtained from data correlation,  $M_T$  is the magma density (mass of solids per unit volume of slurry or solvent in the magma), and  $N$  is the rotational velocity of the impeller or pump rotor. For convenience, either crystal growth rate or mean residence time, both of which are directly related to supersaturation, may be substituted for  $\sigma$  in Eq. (18).

If primary nucleation dominates the process,  $i$  tends to larger values (say greater than 3),  $j$  and  $k$  approach zero, and Eq. (18) approaches Eq. (17). Should crystal-impeller and/or crystal-crystallizer impacts dominate,  $j$  approaches 1; on the other hand, if crystal-crystal contacts dominate,  $j$  approaches 2.

The ease with which nuclei can be produced by contact nucleation is a clear indication that this mechanism is dominant in many industrial crystallization operations. Research on this nucleation mechanism is continuing with the objective of building an understanding of the phenomenon that will allow its successful inclusion in models describing commercial systems.

## D. Fundamentals of Crystal Growth

Crystal growth rates may be expressed as (1) the linear advance rate of an individual crystal face, (2) the change in a characteristic dimension of a crystal, or (3) the rate of change in mass of a crystal or population of crystals. These different expressions are related through crystal geometry; it is often convenient to use the method of measurement as the basis of the growth rate expression or, in certain instances, the method used to analyze a crystallization process will require that growth rate be defined in a specific way. For example, the use of a population balance to describe crystal size distribution requires that growth rate be defined as the rate of change of a characteristic dimension.

Single-crystal growth kinetics involve the advance rate of an individual crystal face normal to itself or the rate of change in crystal size associated with exposure to a super-saturated solution. The advance rate of a single crystal face can be quantified by observation of the face through a calibrated eyepiece of an optical microscope, which allows examination of the structure of the advancing crystal face and isolation of surface-reaction kinetics from mass-transfer kinetics (these phenomena will be discussed later). An additional advantage of single-crystal systems is that it is possible to examine crystal growth kinetics without interference from competing processes such as nucleation.

Multicrystal-magma studies usually involve examination of the rate of change of a characteristic crystal dimension or the rate of increase in the mass of crystals in a magma. The characteristic dimension in such analyses depends upon the method used in the determination of crystal size; for example, the second largest dimension is measured by sieve analyses, while an equivalent spherical diameter is determined by both electronic zone sensing and laser light scattering instruments. A relationship between these two measured dimensions and between the measured quantities and the actual crystal dimensions can be derived from appropriate shape factors. Volume and area shape factors are defined by the equations:

$$v_{\text{crys}} = k_{\text{vol}} L^3 \quad \text{and} \quad a_{\text{crys}} = k_{\text{area}} L^2 \quad (19)$$

where  $v_{\text{crys}}$  and  $a_{\text{crys}}$  are volume and area of a crystal,  $k_{\text{vol}}$  and  $k_{\text{area}}$  are volume and area shape factors, and  $L$  is the characteristic dimension of the crystal. Suppose an equivalent spherical diameter  $L_{\text{sphere}}$  is obtained from an electronic zone-sensing instrument, and the actual dimensions of the crystal are to be calculated. Assume for the sake of this example that the crystals have a cubic shape. Let  $L_{\text{cube}}$  be the edge length of the crystal and  $k_{\text{vol}}^{\text{sphere}}$  and  $k_{\text{vol}}^{\text{cube}}$  be the volume shape factors for a sphere and a cube, respectively. Since the volume of the crystal is the same, regardless of the arbitrarily defined characteristic dimension,

$$v_{\text{crys}} = k_{\text{vol}}^{\text{sphere}} L_{\text{sphere}}^3 = k_{\text{vol}}^{\text{cube}} L_{\text{cube}}^3 \quad (20)$$

Since  $k_{\text{vol}}^{\text{sphere}}$  is  $\pi/6$  and  $k_{\text{vol}}^{\text{cube}}$  is 1.0, the numerical relationship between  $L_{\text{cube}}$  and  $L_{\text{sphere}}$  is given by:

$$L_{\text{cube}} = \left( \frac{k_{\text{vol}}^{\text{sphere}}}{k_{\text{vol}}^{\text{cube}}} \right)^{1/3} L_{\text{sphere}} = \left( \frac{\pi}{6} \right)^{1/3} L_{\text{sphere}} \quad (21)$$

The rate of change of a crystal mass  $dm_{\text{crys}}/dt$  can be related to the rate of change in the crystal characteristic dimension ( $dL/dt = G$ ) by the equation:

$$\frac{dm_{\text{crys}}}{dt} = \frac{d(\rho k_{\text{vol}} L^3)}{dt} = 3\rho k_{\text{vol}} L^2 \left( \frac{dL}{dt} \right) \quad (22)$$

where  $\rho$  is crystal density. Since  $k_{\text{area}} = a_{\text{crys}}/L^2$ ,

$$\frac{dm_{\text{crys}}}{dt} = 3\rho (k_{\text{vol}}/k_{\text{area}}) a_{\text{crys}} G \quad (23)$$

At least two resistances contribute to the kinetics of crystal growth. These resistances apply to (1) integration of the crystalline unit (e.g., solute molecules) into the crystal surface (i.e., lattice), and (2) molecular diffusion or bulk transport of the unit from the surrounding solution to the crystal surface. As aspects of molecular diffusion and mass transfer are covered elsewhere, the current discussion will focus only on surface incorporation.

## 1. Mechanisms

Among the many models that have been proposed to describe surface-reaction kinetics are those that assume crystals grow by layers and others that consider growth to occur by the movement of a continuous step. Each physical model results in a specific relationship between growth rate and supersaturation and, although none can predict growth kinetics *a priori*, insights regarding the effects of process variables on growth can be obtained. Because of the extensive literature on the subject, only the key aspects of the physical models and (in one case) the resulting relationship between growth and supersaturation predicted by each theory will be discussed here.

The model used to describe the growth of crystals by layers is based on a two-step, birth-and-spread mechanism. In one of the steps (birth) a two-dimensional nucleus is formed on the crystal surface, and in the second step (spread) the two-dimensional nucleus grows to cover the crystal surface. When one or the other of the steps is controlling growth rates, simplifications of the more complicated dependence of growth rate on supersaturation can be developed to give what are known as the mononuclear two-dimensional nucleation theory and the polynuclear two-dimensional nucleation theory. In the mononuclear two-dimensional nucleation theory, surface nucleation occurs at a finite rate while the spreading across the surface occurs at an infinite rate. The reverse is true for the polynuclear two-dimensional nucleation theory. Theoretical relationships have been derived between growth rate and supersaturation for each of these conditions but are considered beyond the scope of this discussion.

The screw-dislocation theory (sometimes referred to as the BCF theory because of its development by Burton, Cabrera, and Frank) is based on a mechanism of continuous movement in a spiral or screw of a step or ledge on the crystal surface. The theory shows that the dependence of growth rate on supersaturation can vary from a parabolic relationship at low supersaturations to a linear relationship at high supersaturations. In the BCF theory, growth rate is given by:

$$G = k_G \left( \frac{\epsilon \sigma^2}{b} \right) \tanh \left( \frac{b}{\epsilon \sigma} \right) \quad (24)$$

where  $\epsilon$  is screw dislocation activity and  $b$  is a system-dependent quantity that is inversely proportional to temperature. It can be shown that the dependence of growth rate on supersaturation is linear if the ratio  $b/\epsilon\sigma$  is large, but the dependence becomes parabolic as the ratio becomes small. It is possible, then, to observe variations in the dependence of growth rate on supersaturation for a given crystal-solvent system.

An empirical approach also can be used to relate growth kinetics to supersaturation by simply fitting growth-rate data with a power-law function of the form:

$$G = k_G \sigma^g \quad (25)$$

where  $k_G$  and  $g$  are system-dependent constants. Such an approach is valid over modest ranges of supersaturation, and the power-law function approximates the fundamental expressions derived from the above models.

## 2. Impurities

The presence of impurities can alter growth rates substantially, usually by decreasing them. Furthermore, as described in Section IV.B, impurities can alter crystal morphology through their effects on the growth rates of crystal faces. Mechanisms include: (1) adsorption of an impurity on the crystal surface or at specific growth sites such as kinks, thereby blocking access to the site by a growth unit; (2) formation of complexes between an impurity and a growth unit; and (3) incorporation of an impurity into a growing crystal and creating defects or repelling the addition of a growth unit to the subsequent crystal layer. Few of these mechanistic views result in predictive capabilities, and it is usual to rely on experimental data that are often correlated empirically.

Because impurities most often result in reduced crystal growth rate, feedstocks to laboratory and bench-scale units should be as similar as possible to that expected in the full-scale unit. The generation of impurities in upstream process units can depend on the way those units are operated, and protocols of such units should follow a consistent practice. It is equally important to monitor the composition of recycle streams so as to detect any accumulation of impurities that might lead to a reduction in growth rates.

The solvent from which a material is crystallized influences crystal morphology and growth rate. These effects have been attributed to two sets of factors. One has to do with the effects of solvent on viscosity, density, and diffusivity and, therefore, mass transfer. The second factor is concerned with the structure of the interface between crystal and solvent; a solute-solvent system that has a high solubility is likely to produce a rough interface and, concomitantly, large crystal growth rates.

## E. Crystal Growth in Mixed Crystallizers

Population balances on crystals in a crystallizer require a definition of growth rates in terms of the rate of change of a characteristic dimension:

$$G = \frac{dL}{dt} \quad (26)$$

Furthermore, the solution of a differential population balance requires that the relationship between growth rate and size of the growing crystals be known. When all crystals in the magma grow at a constant and identical rate, the crystal–solvent system is said to follow the McCabe  $\Delta L$  law, while systems that do not are said to exhibit anomalous growth.

Two theories have been used to explain growth-rate anomalies: size-dependent growth and growth-rate dispersion. As with systems that follow the  $\Delta L$  law, anomalous growth by crystals in a multicrystal magma produces crystal populations with characteristic forms. Unfortunately, it is difficult to determine the growth mechanism from an analysis of these forms. This means that either size-dependent growth or growth-rate dispersion may be used to correlate population density data without a certainty that the correct source of anomalous growth has been identified. Determining the actual source of anomalous growth is not trivial, but it may be worthwhile since alignment between a mathematical model and system behavior enhances the utility of the model.

Size-dependent crystal growth results when the rate of growth depends on the size of the growing crystal. Certainly, this may be the case if bulk transport is the controlling resistance to crystal growth, and the literature abounds with expressions for the appropriate mass-transfer coefficients. In the more common situation in which surface integration controls growth rate, there are no mechanistic relationships between growth rate and crystal size, and simple empirical expressions are called upon for that purpose.

Growth-rate dispersion is the term used to describe the behavior of similar sized crystals in the same population exhibiting different growth rates or growth rates that vary with time. The consequences of growth-rate dispersion are illustrated in Fig. 6, which shows the growth of a crystal population that has been immersed in a supersaturated solution. The spread of the distribution increases as the crystal population grows; the slower growing crystals form the tail of the advancing distribution while the faster growing ones form the leading edge. If all crystals in the population grew at the same rate, the distribution would advance uniformly along the size axis. Two causes of growth-rate dispersion have been observed. In one, the growth rate of each crystal in a population is nearly constant, but crystals in the population may grow at a different rate; in the other, the growth rate of an individual crystal fluctuates about a mean value.

The consequences of anomalous growth depends upon the process involved, and this will be pointed out in the discussion on population balances.

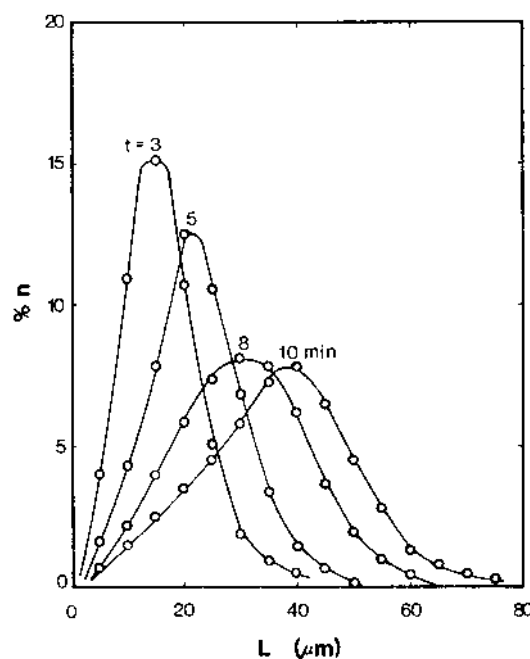


FIGURE 6 Transient population density plot showing growth-rate dispersion.

#### IV. PURITY, MORPHOLOGY, AND SIZE DISTRIBUTIONS

Crystal properties can be divided into two categories: those based on the individual crystal and those involving all crystals of a given population. The three characteristics of the section title compose what is often called *crystal quality*. They represent, along with yield, the most important criteria in the operation of a crystallizer. In the following discussion, some of the factors that influence purity and morphology are described and an introduction is given to methods of quantifying crystal size distributions.

##### A. Crystal Purity

The purity of a crystalline product depends on the nature of the other species in the mother liquor from which the crystals are produced, the physical properties of the mother liquor, and the processing that occurs between crystallization and the final product (downstream processing). Impurities can find their way into the final product through a number of mechanisms: the formation of occlusions, trapping of mother liquor in physical imperfections of the crystals or agglomerates, adsorption of species onto crystal surfaces, as part of chemical complexes (hydrates or solvates), or through lattice substitution.

Occlusions find their way into the crystal structure when the supersaturation in close proximity to the crystal surface is high enough to lead to an unstable surface. Such instability leads to the creation of dendrites, which then join to trap mother liquor in pools of liquid within the crystal. Occlusions are often visible and can be avoided through careful control of the supersaturation in the crystallizer.

Mother liquor can be flushed from a cake of crystals on a filter or centrifuge by washing with a liquid that also may dissolve a small portion of the cake mass. To be effective, the wash liquid must be spread uniformly over the cake and flow through the porous material without significant channeling. Such washing is hindered when the crystals themselves have significant cracks, crevices, or other manifestations of breakage or the mother liquor has a viscosity that is significantly greater than the wash liquid. In the latter event, significant channeling (also called *fingering*) may reduce the effectiveness of the wash process.

Lattice substitution requires that the incorporated impurity be of similar size and function to the primary crystallizing species. In other words, the impurity must fit into the lattice without causing significant dislocations. An example of such a system is found in the crystallization of L-isoleucine in the presence of trace quantities of L-leucine. The two species have similar molecular structures, differing only by one carbon atom in the position of a methyl side group. In this system, the incorporation of L-leucine in L-isoleucine crystals is proportional to the concentration of L-leucine in the mother liquor. Moreover, the shape of the recovered crystals changes as the content of L-leucine in recovered crystal increases.

## B. Crystal Morphology

Both molecular and macroscopic concepts are important in crystal morphology. Molecular structures (i.e., the arrangements of molecules in specific lattices) can greatly influence the properties of a crystalline species and variations from a single structure lead to the prospect of polymorphic systems. In such systems, the molecular species of the crystal can occupy different locations depending on the conditions at which the crystal is formed, and both microscopic and macroscopic properties of the crystal can vary depending on the polymorph formed. There is, in general, a single stable polymorph for prevailing conditions, but that polymorph may not have been formed during the crystallization process. In such cases, system thermodynamics will tend to force transformation from the unstable polymorph to the stable one at rates that may vary from being nearly instantaneous to infinitely slow. Additional discussion of the molecular structures of crystalline materials has been provided elsewhere.

The characteristic macroscopic shape of a crystal results, in large measure, from the internal lattice structure; surfaces are parallel to planes formed by the constituent units of the crystal. Moreover, although the Law of Constant Interfacial Angles is a recognition that angles between corresponding faces of all crystals of a given substance are constant, the faces of individual crystals of that substance may exhibit varying degrees of development. As a result, the general shape or habit of a crystal may vary considerably.

Crystal morphology (i.e., both form and shape) affects crystal appearance; solid-liquid separations such as filtration and centrifugation; product-handling characteristics such as dust formation, agglomeration, breakage, and washing; and product properties such as bulk density, dissolution kinetics, catalytic activity, dispersability, and caking.

The shape of a crystal can vary because the relative rates of growth of crystal faces can change with system conditions; faster growing faces become smaller than faces that grow more slowly and in the extreme may disappear from the crystal altogether. For illustration, consider the two-dimensional crystal shown in Fig. 7a and the process variables that would cause the habit to be modified to the forms shown in Figs. 7b and c. The shape of the crystal depends on the ratio of the growth rate of the horizontal faces,  $G_h$ , to the growth rate of the vertical faces,  $G_v$ . For the shapes shown in Fig. 7,

$$\left(\frac{G_h}{G_v}\right)_b < \left(\frac{G_h}{G_v}\right)_a < \left(\frac{G_h}{G_v}\right)_c \quad (27)$$

Growth rates depend on the presence of impurities, system temperature, solvent, mixing, and supersaturation, and the importance of each may vary from one crystal face to another. Consequently, an alteration in any or all of these variables can result in a change of the crystal shape.

Modeling intermolecular and intramolecular interactions through molecular mechanics calculations has advanced significantly in the past decade, and it has provided the basis for prediction of the equilibrium shape of

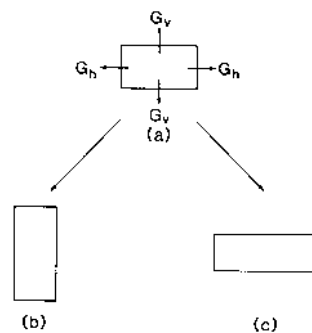


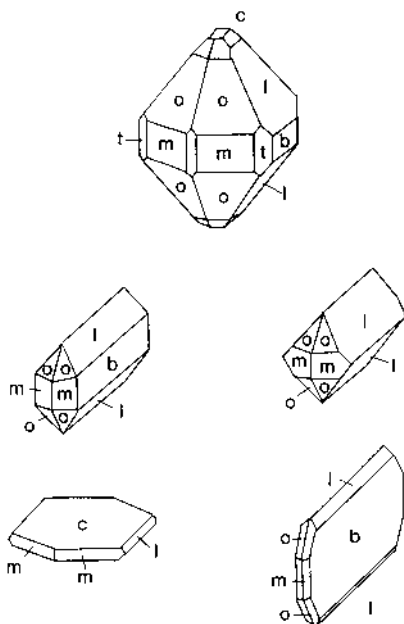
FIGURE 7 Effect of facial growth rates on crystal shape.

a known crystalline species. While not yet uniformly successful on a quantitative basis, the definition and modeling of crystal lattice potential energy equations has provided an understanding of crystal growth and morphology on the molecular level. Derivation of external crystal morphology from internal lattice structures via simulation has been proven possible for several organic compounds. Numerical minimization techniques, coupled with the appropriate valence and nonbonded energy expressions, have enabled accurate determination of favorable molecular arrangements within a wide variety of molecular crystals.

The shape of crystals obtained as a result of following a specific crystallization protocol may be unsatisfactory and, as a result, methods for modifying the habit of considerable interest. The predictive capabilities cited in the preceding paragraph are of great utility in such an instance as they may be used to determine factors leading to the unsatisfactory shape and guide subsequent experiments in which a more desirable shape is sought. Inevitably, such a search involves extensive laboratory or bench-scale experiments to determine processing variations that will lead to a desired crystal shape.

As an example of the variations in shape that can be exhibited by a single crystalline material, consider the forms of potassium sulfate shown in Fig. 8. Clearly, the processing characteristics and particulate properties of the differently shaped potassium sulfate crystals will vary.

The mechanisms and variables affecting crystal shape can be categorized as follows:



**FIGURE 8** Shapes of  $K_2SO_4$  crystals. [From Mullin, J. W. (1993). "Crystallization," 3rd ed. Butterworth-Heinemann, London. With permission.]

## 1. Intrinsic growth rates

- a. *Temperature*: The growth rates of individual crystal faces depend on temperature, typically following an Arrhenius rate law:

$$G = G_0 \exp\left(-\frac{\Delta E_G}{RT}\right) \quad (28)$$

If different crystal faces have different activation energies, variation of the temperature at which crystallization takes place modifies individual growth rates to varying degrees and results in a modified crystal shape.

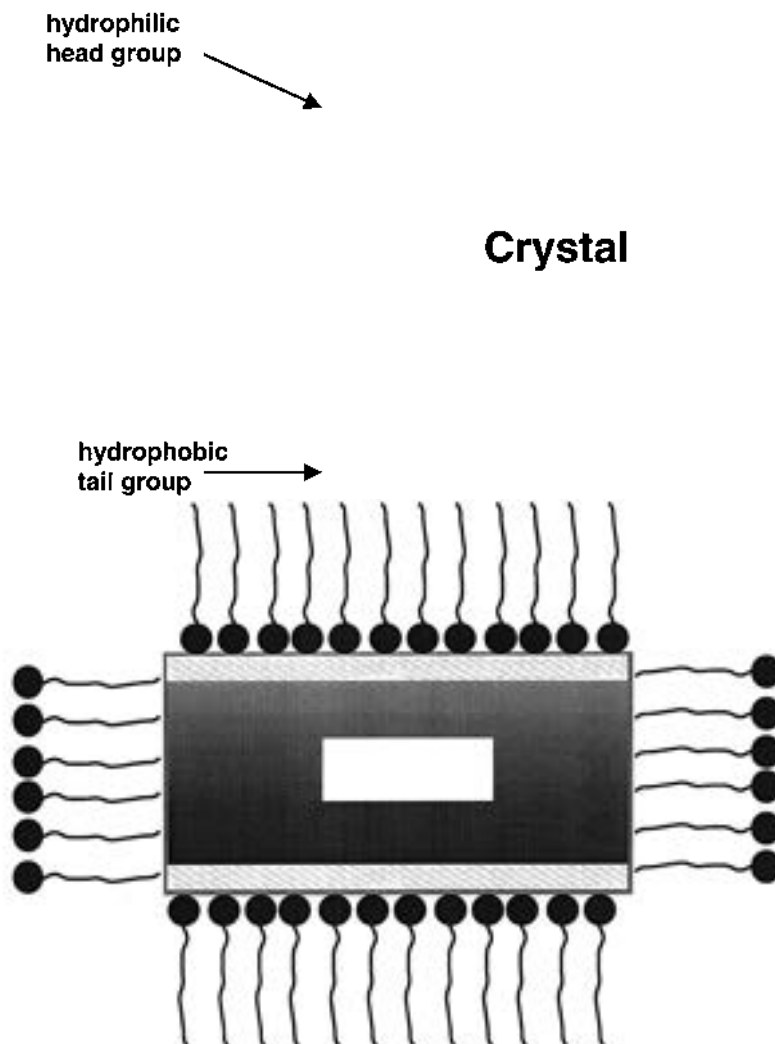
- b. *Mixing*: The intensity of mixing may determine the degree to which bulk mass transfer is involved in growth kinetics, and this can influence the resulting crystal shape.
- c. *Supersaturation*: The dependence of growth kinetics on supersaturation may vary from one crystal face to another. Accordingly, different prevailing supersaturations can lead to different crystal shapes.

## 2. Interfacial behavior

- a. *Solvent*: Different solvents exhibit different interactions with crystal faces and can alter crystal shape. A change in solvent also can alter the stoichiometry of the crystal (e.g., from a hydrate to an anhydrate stoichiometry), which can produce crystals with quite different morphology.
- b. *Surfactants*: Addition of a surfactant to a crystallizing system can influence the crystal shape in a manner illustrated schematically in Fig. 9. Here, surfactant molecules are shown being attracted to crystal faces in varying ways; the hydrophilic head groups favor the horizontal faces, while the hydrophobic tail groups are preferentially attracted to the vertical faces. A growth unit must displace the surfactant to approach a growing crystal face. As hydrophilic interactions are typically much stronger than hydrophobic ones, the growth unit preferentially enters the vertical faces and growth in the horizontal direction is favored.

## 3. Access to growth site

- a. *Blockage by species attracted to growth site*: Impurities may preferentially locate at a kink or other favored growth site and block growth at that site. A difference in the character of the kink or growth site from one face to another could result in modification of the crystal shape.
- b. *Species partially fitting into crystal lattice*: In these instances, an impurity molecule is comprised of two parts, one that fits into the crystal lattice



**FIGURE 9** Attachment of surfactant molecules to crystal surfaces.

and a second that does not. The part that does not fit repulses incoming growth units or causes significant interatomic stress because of its position in the crystal lattice. If such species are purposely added to the crystallizing system to modify crystal morphology, they are referred to as tailor-made additives.

### C. Crystal Size Distributions

Most crystallization processes produce particles whose sizes cover a range of varying breadth. If the particles consist of single crystals, the resulting distribution is a crystal size distribution (CSD); on the other hand, if the particles consist of agglomerates or other combination of multiple crystals, the distribution is a particle size distribution. In either case, the distribution is expressed in terms of either population (number) or mass. The popu-

lation distribution relates the number of crystals at each size to the size, while the mass distribution expresses how mass is distributed over the size range. In the following paragraphs, methods for describing and using distribution functions will be outlined.

Size distribution is a major determinant of the properties of crystalline products, especially appearance, and to downstream processing and handling of crystalline materials. Solid-liquid separation by filtration or centrifugation can be straightforward with a desired CSD, but it can be disastrous when an inappropriate one increases resistance to liquor flow through a filter or centrifuge cake. Likewise, CSD affects other downstream processing such as the removal of impurities and mother liquor by washing, dissolution or reaction of the crystals, and transporting or storing crystals.

Crystal size distributions may be expressed by: (1) histograms, which are the amount or fraction of mass or



**TABLE II Sieved KNO<sub>3</sub> Crystals from Hypothetical 1-Liter Sample**

Sieve no., <i>i</i>	<i>L</i> (μm)	$\Delta M_i$ (g/L)	<i>M(L)</i> (g/L)	<i>F(L)</i> (frac)	$\bar{L}_i$ (μm)	$\Delta N_i$ (no./L)	<i>N(L)</i> (frac)	<i>m</i> (g/μm·L)	<i>n</i> (no./μm·L)
1	707	0	32.974	1.000		1611			
2	500	7.296	25.678	0.779	603.5	16	1595	0.0352	0.076
3	354	11.512	14.166	0.430	427.0	70	1525	0.0789	0.480
4	240	9.011	5.154	0.156	297.0	163	1362	0.0790	1.430
5	177	3.145	2.009	0.061	208.5	164	1198	0.0499	2.610
6	125	1.322	0.687	0.021	151.0	182	1016	0.0254	3.500
7	88	0.462	0.225	0.007	106.5	181	834	0.0125	4.900
8	63	0.159	0.066	0.002	75.5	175	659	0.0064	7.000
9	44	0.055	0.011	0.000	53.5	171	488	0.0029	9.000
10	0	0.011	0.000	0.000	22.0	488	0	0.0002	11.100
Total		32.974				1611			

number over each increment in size; (2) cumulative distributions, which are the total or fraction of mass or number below (or above) a given size; and (3) density functions, which are the derivatives (with respect to size) of cumulative distributions. These definitions will be illustrated by considering a hypothetical potassium nitrate system from which a 1-liter slurry sample has been withdrawn, filtered, washed, dried, and sieved to give the results shown in Table II.

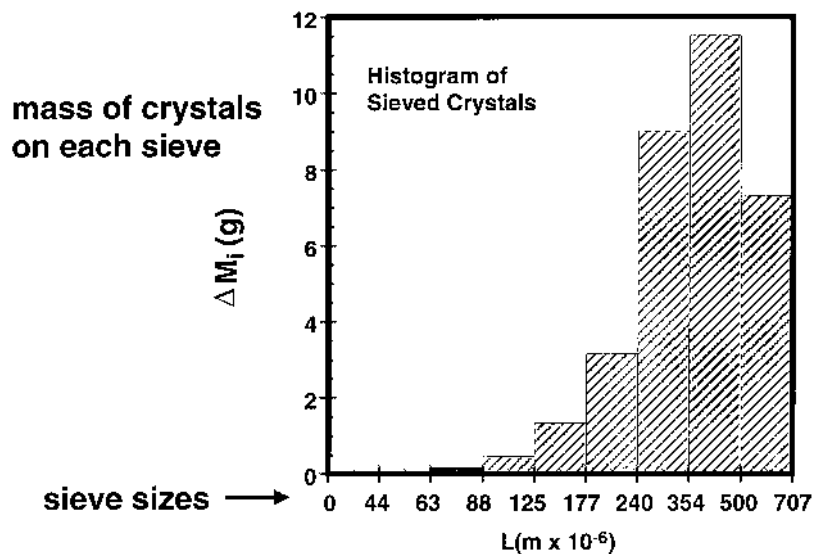
The first three and the sixth columns give the sieve data and should be read as follows: All of the sieved matter passed through the 707-μm sieve, and 7.296 g remained on the 500-μm sieve and had an arithmetic average size of 603.5 μm. Similar descriptions can be given for crystals that remained on the other sieves and pan ( $L = 0$ ). The total crystal mass recovered was 39.974 g. A histogram of the mass distribution from these data is shown in Fig. 10.

The method by which crystals are sized gives either number or mass of crystals in a given size range. The sieve analysis in the above example gives mass distributions, so that the histogram is constructed in terms of crystal mass, and a cumulative mass distribution,  $M(L)$ , can be defined as the mass of crystals in the sample passing through the sieve of size  $L$ . In other words,

$$M(L) = \sum_{L=0}^{L(i)} \Delta M_i \quad (29)$$

Such calculations give the mass of crystals below size  $L$ , and the results are shown in column 4 of Table II. Column 5 gives the cumulative mass fraction distribution:

$$F(L) = \frac{M(L)}{M_{\text{total}}} \quad (30)$$

**FIGURE 10** Histogram of size distribution from example.



Transforming a mass distribution to a number distribution, or vice versa, requires a relationship between the measured and desired quantities. The mass of a single crystal,  $m_{\text{crys}}$ , is related to crystal size by the volume shape factor,  $k_{\text{vol}}$  (see Eq. (19)):

$$m_{\text{crys}} = \rho k_{\text{vol}} L^3 \quad (31)$$

Consequently, the number of crystals on a sieve in the example,  $\Delta N_i$ , can be estimated by dividing the total mass on sieve  $i$  by the mass of an average crystal on that sieve. If the crystals on that sieve are assumed to have a size equal to the average of the sieve through which they have passed and the one on which they are held,  $\bar{L}_i = (L_{i-1} + L_i)/2$ , then:

$$\Delta N_i = \frac{\Delta M_i}{\rho k_{\text{vol}} \bar{L}_i^3} \quad (32)$$

Potassium nitrate crystals have a density of  $2.11 \times 10^{-12} \text{ g}/\mu\text{m}^3$ , which allows for the determination of the estimated crystal numbers on each sieve in Table II. A cumulative number distribution,  $N(L)$ , and a cumulative number fraction distribution,  $F(L)$ , can be calculated using methods similar to those for calculating  $M(L)$  and  $W(L)$ .

Mass and population densities are estimated from the respective cumulative number and cumulative mass distributions:

$$m(\bar{L}) = \frac{\Delta M_i}{\Delta L_i} \quad (33)$$

$$n(\bar{L}) = \frac{\Delta N_i}{\Delta L_i} \quad (34)$$

So that if  $\Delta L_i \rightarrow 0$ ,

$$m(L) = \frac{dM(L)}{dL} \Rightarrow M(L) = \int_0^L m dL \quad (35)$$

and

$$n(L) = \frac{dN(L)}{dL} \Rightarrow N(L) = \int_0^L n dL \quad (36)$$

Equations (33) and (34) are used to obtain the last two columns of Table II.

In the example, all of the results are for the given sample size of 1 liter and the quantities estimated have units reflecting that basis. This basis volume is arbitrary, but use of the calculated quantities requires care in defining this basis consistently in corresponding mass and population balances. The volume of clear liquor in the sample is an alternative, and sometimes more convenient, basis.

Moments of a distribution provide information that can be used to characterize particulate matter. The  $j$ th moment of the population density function  $n(L)$  is defined as:

$$m_j = \int_0^\infty L^j n(L) dL \quad (37)$$

From Eq. (37), it can be demonstrated that the total number of crystals, the total length, the total area, and the total volume of crystals, all in a unit of sample volume, can be evaluated from the zeroth, first, second, and third moments of the population density function. Moments of the population density function also can be used to estimate number-weighted, length-weighted, area-weighted, and volume- or mass-weighted quantities. These averages are calculated from the general expression:

$$\bar{L}_{j+1,j} = \frac{m_{j+1}}{m_j} \quad (38)$$

where  $j = 0$  for a number-weighted average, 1 for a length-weighted average, 2 for an area-weighted average, and 3 for a volume- or mass-weighted average.

Crystal size distributions may be characterized usefully (though only partially) by a single crystal size and the spread of the distribution about that size. For example, the dominant crystal size represents the size about which the mass in the distribution is clustered. It is defined as the size,  $L_D$ , at which a unimodal mass density function is a maximum, as shown in Fig. 11; in other words, the dominant crystal size  $L_D$  is found where  $dm/dL$  is zero. (The data used to construct Fig. 11 are from Table II.) As the mass density is related to the population density by:

$$m = \rho k_v n L^3 \quad (39)$$

the dominant crystal size can be evaluated from the population density by:

$$\frac{d(nL^3)}{dL} = 0 \quad \text{at} \quad L = L_D \quad (40)$$

The spread of the mass-density function about the dominant size is the coefficient of variation (c.v.) of the CSD.

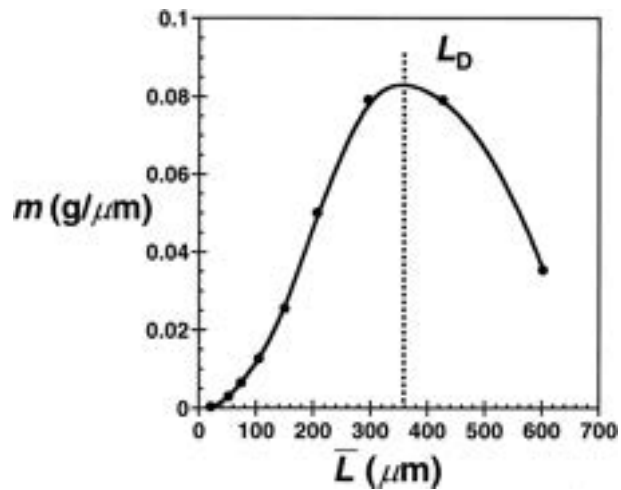


FIGURE 11 Mass-density function with single mode showing dominant size.

It is defined by:

$$\text{c.v.} = \frac{\sigma}{L_D} \quad (41)$$

and estimated from the moments of the distribution:

$$\text{c.v.} = \left[ \frac{m_3 m_5}{m_4^2} - 1 \right]^{1/2} \quad (42)$$

This is especially useful for systems that cannot be described by an analytical distribution function.

## V. CRYSTALLIZER CONFIGURATION AND OPERATION

Crystallization equipment can vary in sophistication from a simple stirred tank to a complicated multiphase column, and the protocol can range in complexity from simply allowing a vat of liquor to cool to the careful manipulation required of batch cyclic operations. In principle, the objectives of these systems are the same: to produce a product meeting specifications on quality at an economical yield. This section will examine some of the considerations that go into the selection of a crystallizer so as to meet these objectives.

One of the first decisions that must be made is whether the crystallizer operation is to be batch or continuous. In general, the advantages of each type of operation should be weighed in choosing one over the other, but more often the decision rests on whether the other parts of the process are batch or continuous. If they are batch, then it is likely that the crystallizer also should be batch.

The equipment required for batch crystallization can be very simple. For example, some crystalline materials are produced by simply allowing a charge of hot liquor to cool. After the crystals have formed, the magma is discharged through a filter or the liquor may be decanted and the settled slurry filtered. Very large crystals can be obtained by allowing encrustations formed on the walls of these crystallizers to grow undisturbed; after the system has come to equilibrium, the liquor is drained and the crystals are removed by scraping them from the surface.

Batch crystallizers can be used in a campaign to produce a particular product and in a second campaign to produce another product. Generally, it is not possible to operate continuous processes in this way. Batch crystallizers can handle viscous or toxic systems more easily than can continuous systems, and interruption of batch operations for periodic maintenance is less difficult than dealing with interruptions in continuous processes. The latter factor may be especially important in biological processes that require frequent sterilization of equipment. Batch crystallizers can produce a narrow crystal size distribution, whereas special processing features are required to narrow the distribu-

tion obtained from a continuous crystallizer. The effects of operating variables on crystal size distributions will be discussed in Section VI.

The throughput per unit crystallizer volume is greater for a continuous system. Batch units have several operating steps in a cycle—charging, heating or cooling, crystallizing, discharging, and cleaning—and the unit production rate is based on the total cycle time, even though the formation of crystals may occur only during a small portion of the cycle.

It may be easier to operate a continuous system so that it reproduces a particular crystal size distribution than it is to reproduce crystal characteristics from a batch unit. Moreover, the coupling of several transient variables and nucleation make it difficult to model and control the operation of a batch crystallizer.

### A. Relationship of Solubility to Mode of Operation

The driving force for crystal formation can be generated through a variety of means, including cooling or heating to reduce or increase the system temperature, evaporating solvent, evaporative (flash) cooling, inducing a chemical reaction (when the reaction product is sparingly soluble, the process is called *precipitation*), adjusting pH, salting out through the addition of a nonsolvent, direct-contact cooling with a refrigerant, or some other means. All of these modes of operation can be implemented in either a batch or a continuous process. In addition, two or more of the modes may be combined to enhance the product yield.

As discussed in an earlier section, solubility is intrinsic to the solute-solvent system, and the relationship of solubility to temperature often determines the mode by which a crystallizer is operated. Recall for example that the solubility of NaCl (see Fig. 2) is essentially independent of temperature, while  $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$  has a solubility that exhibits a strong dependence on temperature. Consequently, cooling a sodium chloride solution cannot generate significant product yield; solvent evaporation is the primary mode of NaCl production. On the other hand, reducing the temperature of a saturated solution of sodium sulfate generates substantial product and may be used alone or in combination with evaporation.

Cooling crystallizers utilize a heat sink to remove both the sensible heat from the feed stream and the heat of crystallization released or, in some cases absorbed, as crystals are formed. The heat sink may be no more than the ambient surroundings of a batch crystallizer, or (as is more likely) it may be cooling water or another process stream.

Evaporative crystallizers generate supersaturation by removing solvent from the mixture, thereby increasing the solute concentration. They may be operated under vacuum, and in those circumstances it is necessary to have a

vacuum pump or ejector as a part of the unit. If the boiling point elevation—the increase in boiling temperature due to the presence of the solute—is low, mechanical recompression of the vapor obtained from solvent evaporation may be used in some cases to produce a heat source to drive the operation.

Evaporative-cooling crystallizers are fed with a liquor whose temperature is such that solvent flashes upon feed entry to the crystallizer. They typically are operated under vacuum, and flashing of solvent increases the solute concentration in the remaining liquor while simultaneously reducing the temperature of the magma. The mode of this operation can be reduced to that of a simple cooling crystallizer by returning condensed solvent to the crystallizer body.

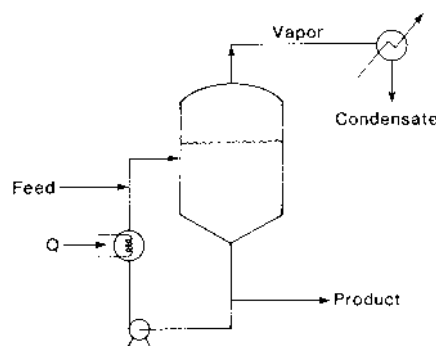
Salting-out crystallization operates through the addition of a nonsolvent to the magma in a crystallizer. The selection of the nonsolvent is based on the effect of the solvent on solubility, cost, properties that affect handling, interaction with product requirements, and ease of recovery. Adding a nonsolvent to the system increases the complexity of the process; it increases the volume required for a given residence time and produces a highly nonideal mixture of solvent, nonsolvent, and solute.

Melt crystallization operates with heat as a separating agent, but a crystalline product is not generated in the process. Instead, crystals formed during the operation are remelted and the melt is removed as the product. Such operations are often used to perform the final purification of products after prior separation units; for example, the purity of an acrylic acid feed may be increased from 99.5 to 99.9%. Melt crystallizers do not require solids handling units nor do they utilize solid–liquid separation equipment. Finally, in some instances the use of melt crystallization can eliminate the use of solvents, thereby reducing the environmental impact of the process.

## B. Crystallizers

The basic requirements of a crystallization system are (1) a vessel to provide sufficient residence time for crystals to grow to a desired size, (2) mixing to provide a uniform environment for crystal growth, and (3) a means of generating supersaturation. Crystallization equipment is manufactured and sold by several vendors, but some chemical companies design their own crystallizers based on expertise developed within their organizations. Rather than attempt to describe the variety of special crystallizers that can be found in the marketplace, this section will provide a brief general survey of types of crystallizers that utilize the modes outlined above.

The forced-circulation crystallizer is a simple unit designed to provide high heat-transfer coefficients in either an evaporative or a cooling mode. Figure 12 shows a

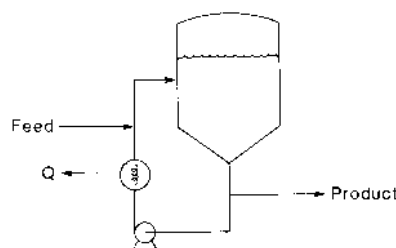


**FIGURE 12** Schematic diagram of a forced-circulation evaporative crystallizer.

schematic diagram of an evaporative forced-circulation crystallizer that withdraws a slurry from the crystallizer body and pumps it through a heat exchanger. Heat transferred to the circulating magma causes evaporation of solvent as the magma is returned to the crystallizer. This type of unit is used to control circulation rates and velocities past the heat transfer surfaces, and the configuration shown is especially useful in applications requiring high rates of evaporation. A calandria that provides heat transfer through natural convection is an alternative to forced-circulation systems.

Scale formation on the heat exchanger surfaces or at the vapor–liquid surface in the crystallizer can cause operational problems with evaporative crystallizers. These can be overcome by avoiding vaporization or excessive temperatures within the heat exchanger and by properly introducing the circulating magma into the crystallizer. For example, introducing the circulating magma a sufficient distance below the surface of the magma in the crystallizer prevents vaporization upon re-entry and forces it to occur at a well-mixed zone above the point of re-entry. Alternatively, the magma may be introduced so as to induce a swirling motion that dislodges encrustations from the wall of the crystallizer at the vapor–liquid interface.

Figure 13 shows a schematic diagram illustrating the configuration of a surface cooling (indirect heat transfer) crystallizer. Heat can be transferred to a coolant in an external heat exchanger, as shown, or in coils or a jacket



**FIGURE 13** Schematic diagram of a forced-circulation, surface-cooling crystallizer.

within the crystallizer. An external cooling surface requires the use of a circulation pump, but this expense may be mitigated by obtaining a higher heat-transfer coefficient than would result with the use of coils or a jacketed vessel. The rate of heat transfer  $Q$  from the circulation loop of a cooling crystallizer must be sufficient to reduce the temperature of the feed and to remove the heat of crystallization of the solute. Assuming that no substantial crystallization occurs in the heat exchanger and limiting the difference between entering and leaving temperatures of the circulating magma ( $T_{in} - T_{out}$ ), so as to minimize formation of encrustations, the required magma circulation rate  $\dot{m}_{circ}$  can be determined from the equation:

$$\dot{m}_{circ} = \frac{Q}{[C_P(T_{in} - T_{out})]_{circ}} \quad (43)$$

where  $C_P$  is the heat capacity of the circulating magma. The methods by which  $Q$  can be evaluated were discussed in Section II. It is not uncommon to limit the decrease in magma temperature to about 3 to 5°C; therefore, both the circulation rate and heat-transfer surface must be large.

The feed to cooling crystallizers should be rapidly mixed with the magma so as to minimize the occurrence of regions of high supersaturation. Such regions lead to excessive nucleation, which is detrimental to the crystal size distribution. The type of pump used in the circulation loop also can lead to degradation of the crystal size distribution; an inappropriate pump causes crystal attrition through abrasion, fracture, or shear, and most commercial systems use specially designed axial-flow pumps that provide high flow rates and low shear.

Direct-contact refrigeration can be used if either the operating temperature of the crystallizer is low in comparison to the temperature of available cooling water or there are severe problems with encrustations. In such an operation, a refrigerant is mixed with the crystallizer contents and vaporized at the magma surface. On vaporizing, the refrigerant removes sufficient heat from the magma to cool the feed and to remove the heat of crystallization. The refrigerant vapor must be compressed, condensed, and recycled for the process to be economical. Moreover, the refrigerant must be insoluble in the liquor to minimize losses and product contamination.

Special devices for classification of crystals may be used in some applications. Figure 14 shows a draft-tube-baffle (DTB) crystallizer that is designed to provide preferential removal of both fines and classified product. As shown, feed is introduced to the fines circulation line so that any nuclei formed upon introduction of the feed can be dissolved as the stream flows through the fines-dissolution heat exchanger. The contents of the crystallizer are mixed by the impeller, which forces the slurry to flow in the indicated direction. A quiescent zone is formed between the

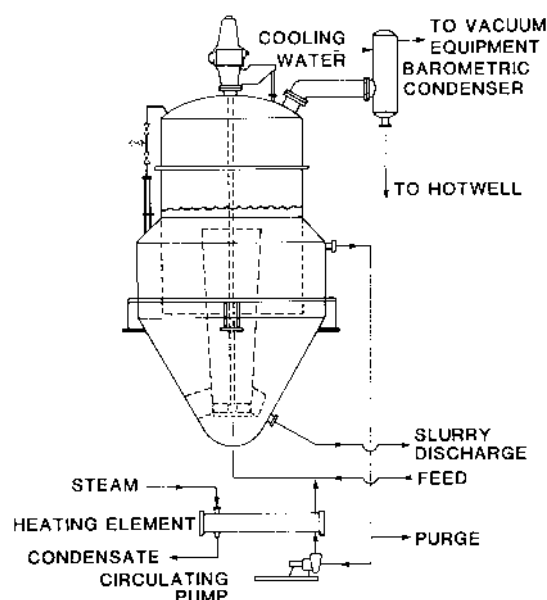


FIGURE 14 Draft-tube-baffle crystallizer. [Courtesy of Signal Swenson Division.]

baffle extending into the chamber and the outside wall of the crystallizer. Flow through the quiescent zone can be adjusted so that crystals below a certain size (determined by settling velocity) are removed in the fines-dissolution circuit. In the elutriation leg, crystals below a certain size are preferentially swept back into the crystallizer by the flow of recycled mother liquor; accordingly, larger crystals, which have a higher settling velocity, are removed preferentially from the system.

A second major type of crystallizer with special channeling devices is comprised of those having configurations like the Oslo crystallizer shown in Fig. 15. The objective of this unit is to form a supersaturated solution by evaporation in the upper chamber and to have crystal growth in the lower (growth) chamber. The use of the downflow pipe in the crystallizer provides good mixing in the growth chamber. As shown, the lower chamber has a varying diameter, which can provide some internal classification of crystals. The lowest portion of the chamber has the smallest diameter and can be considered perfectly mixed; as the chamber diameter increases, the upward velocity of the slurry decreases and larger crystals tend to settle. In principle, only small crystals are supposed to leave the chamber in the circulating slurry, to flow through the circulation pump, and to enter the upper chamber. As the probability of a crystal colliding with the impeller decreases with decreasing crystal size, the internal classification provided by the Oslo crystallizer could provide some control of contact nucleation.

Melt crystallizers can be operated in a variety of ways. In one, feed enters the crystallizer and contacts a slurry

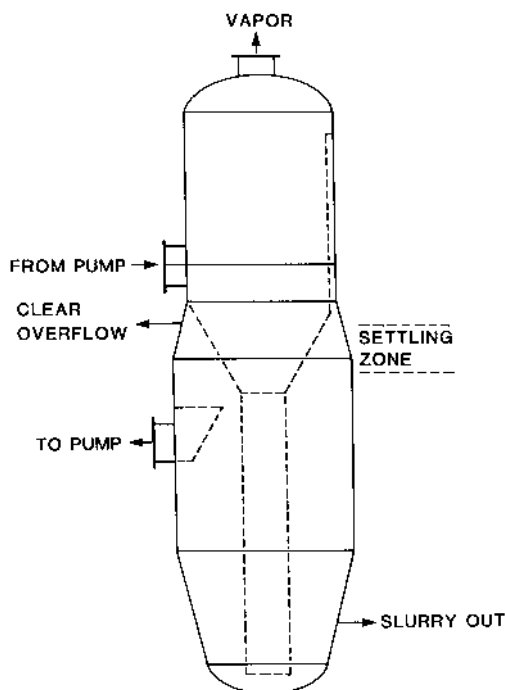


FIGURE 15 Oslo crystallizer.

of mother liquor and crystals of the desired product. The crystals are forced to move in a specific direction by gravity or rotating blades. As they flow towards the appropriate end of the crystallizer, the crystals encounter a heated region and are melted. A portion of the melt is removed as product, while the remainder flows countercurrently to the crystals, thereby providing some refining and removing impure adhering liquid.

In a second method of operation, the feed material is circulated through a bank of tubes, each of which has a diameter of up to about 8 cm. The walls of the tubes are cooled, and material crystallizes on them throughout a fixed operating period. At the end of that period, the remaining liquid is sent to a holding tank for further processing, and then the tubes are heated slowly to cause partial melting of the adhering solids. This step is known as “sweating,” and the impure “sweated” liquid produced is removed from the crystallizer and held for further processing. Finally, the product is obtained by adding additional heat to the tubes and melting the remaining adhering solids. The actual sequencing of these steps and the reprocessing of residual and sweated liquids may be quite complicated.

## VI. POPULATION BALANCES AND CRYSTAL SIZE DISTRIBUTIONS

A balance on the population of crystals in a crystallizer can be used to relate process variables to the crystal size

distribution of the product or intermediate material. Such balances are not independent of those on mass and energy, and their solution requires an independent expression for nucleation kinetics.

In formulating a population balance, crystals are assumed sufficiently numerous for the population distribution to be treated as a continuous function. One of the key assumptions in the development of a simple population balance is that all crystal properties, including mass (or volume), surface area, and so forth are defined in terms of a single crystal dimension referred to as the characteristic length. For example, Eq. (19) relates the surface area and volume of a single crystal to a characteristic length  $L$ . In the simple treatment provided here, shape factors are taken to be constants. These can be determined by simple measurements or estimated if the crystal shape is simple and known—for example, for a cube  $k_{\text{area}} = 6$  and  $k_{\text{vol}} = 1$ .

The beginning point for any balance is the following statement:

$$\begin{aligned} \text{input} + \text{generation} - \text{output} - \text{consumption} \\ = \text{accumulation} \end{aligned} \quad (44)$$

where each of the terms may be expressed as a rate or an amount. In a population balance, the number of entities (such as crystals) is the balanced quantity and each of the terms has dimensions of number of crystals per unit time for a differential balance or number of crystals for an integral balance. The principles involved in formulating a balance are outlined in the following sections, and they provide guidance in developing corresponding balances for systems whose configurations do not conform to those described here.

### A. Perfectly Mixed, Continuous Crystallizers

The balance equation must be constructed for a control volume, which for a perfectly mixed crystallizer may be assumed to be the total volume of the crystallizer  $V_T$ . Then, a balance on the number of crystals in any size range (say,  $L_1$  to  $L_2 = L_1 + \Delta L$ ) must account for crystals that enter and leave that size range by: (1) convective flow, (2) crystal growth, (3) crystal agglomeration, and (4) crystal breakage. Agglomeration and breakage can be detected through careful inspection of product particles, and they can be quite significant in some processes. For simplicity, however, they will be assumed negligible in the present analysis. The rate of crystal growth  $G$  will be defined as in Eq. (26); i.e., the rate of change of the characteristic crystal dimension  $L$ :

$$G = \frac{dL}{dt}$$

Then,

$$\text{growth rate into the size range} = V_T(Gn)_{L_1} \quad (45)$$

$$\text{growth rate out of the size range} = V_T(Gn)_{L_2} \quad (46)$$

$$\text{removal rate of crystals in the size range} = V_{\text{out}} \int_{L_1}^{L_2} n dL \quad (47)$$

$$\text{feed rate of crystals in the size range} = V_{\text{in}} \int_{L_1}^{L_2} n_{\text{in}} dL \quad (48)$$

$$\text{accumulation rate in the crystallizer} = \frac{\partial}{\partial t} \int_{L_1}^{L_2} n V_T dL \quad (49)$$

Substituting the terms from Eqs. (46) through (49) into Eq. (44) gives:

$$\begin{aligned} V_T(Gn)_{L_1} + V_{\text{in}} \int_{L_1}^{L_2} n_{\text{in}} dL \\ = V_T(Gn)_{L_2} + V_{\text{out}} \int_{L_1}^{L_2} n dL + \frac{\partial}{\partial t} \int_{L_1}^{L_2} n V_T dL \end{aligned} \quad (50)$$

Manipulation of this equation leads to

$$\frac{\partial(nG)}{\partial L} + \frac{V_{\text{out}}n}{V_T} - \frac{V_{\text{in}}n_{\text{in}}}{V_T} = -\frac{\partial n}{\partial t} \quad (51)$$

Equation (51) may be used as a starting point for the analysis of any crystallizer that has a well-mixed active volume and for which crystal breakage and agglomeration can be ignored. As an illustration of how the equation can be simplified to fit specific system behavior, suppose the feed to the crystallizer is free of crystals and that it is operating at steady state. Then,  $n_{\text{in}} = 0$  and  $\partial n / \partial t = 0$ . Now suppose that the crystal growth is invariant with size and time; in other words, assume the system follows the McCabe  $\Delta L$  law and therefore exhibits neither size-dependent growth nor growth-rate dispersion. Then,

$$\frac{\partial(nG)}{\partial L} = G \frac{\partial n}{\partial L} \quad (52)$$

Defining a mean residence time  $\tau = V_T / V_{\text{out}}$  and applying the aforementioned restrictions leads to

$$G \frac{dn}{dL} + \frac{n}{\tau} = 0 \quad (53)$$

( $\tau$  is often referred to as the drawdown time to reflect the fact that it is the time required to empty the contents from the crystallizer.) Integrating Eq. (53) with the boundary condition  $n = n^\circ$  at  $L = 0$ :

$$n = n^\circ \exp\left(-\frac{L}{G\tau}\right) \quad (54)$$

If the crystallizer has a clear feed, growth is invariant, but if the magma volume  $V_T$  is allowed to vary, the population balance gives:

$$\frac{\partial n}{\partial t} + \frac{\partial(nG)}{\partial L} + n \frac{\partial(\ln V_T)}{\partial t} + \frac{V_{\text{out}}n}{V_T} = 0 \quad (55)$$

The system model that led to the development of the last two equations is referred to as the mixed-suspension, mixed-product removal (MSMPR) crystallizer.

Under steady-state conditions, the rate at which crystals are produced by nucleation must be equal to the difference in rates at which crystals leave and enter the crystallizer. Accordingly, for a clear feed,

$$V_T B^\circ = V_{\text{out}} \int_0^\infty n dL \Rightarrow B^\circ = \frac{1}{\tau} \int_0^\infty n dL \quad (56)$$

For crystallizers following the constraints given above,

$$B^\circ = n^\circ G \quad (57)$$

For a given set of crystallizer operating conditions, nucleation and growth rates can be determined by measuring the population density of crystals in a sample taken from either the well-mixed zone of a crystallizer or the product stream flowing from that zone. Sample analyses are correlated with Eqs. (54) and (57), and nucleation and growth rates are determined from those correlations. The sample must be representative of the crystal population in the crystallizer (or leaving the well-mixed unit), and experience with such measurements is invaluable in performing this analysis properly. Figure 16 shows a plot of

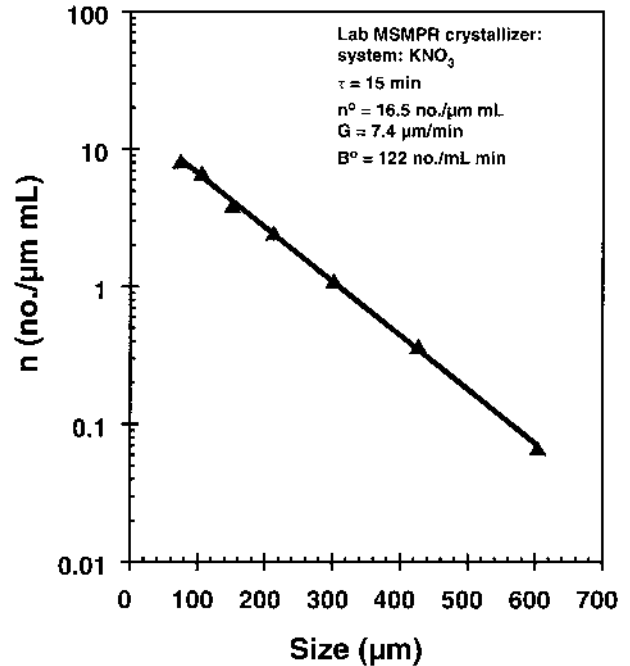


FIGURE 16 Typical population density plot from perfectly mixed, continuous crystallizer.



typical population density data obtained from a crystallizer meeting the stated assumptions. The slope of the plot of such data may be used to obtain the growth rate while the intercept can be used to estimate nucleation rate.

Many industrial crystallizers operate in a well-mixed or near well-mixed manner, and the equations derived above can be used to describe their performance. Also, the simplicity of the equations describing an MSMR crystallizer make experimental equipment configured so as to meet the assumptions leading to Eq. (54) useful in determining nucleation and growth kinetics. From a series of runs at different operating conditions, correlations of nucleation and growth kinetics with appropriate process variables can be obtained (see, for example, the discussions of Eqs. (18) and (25)). The resulting correlations can then be used to guide either crystallizer scale-up or the development of an operating strategy for an existing crystallizer.

It is often very difficult to measure supersaturation, especially in systems that have high growth rates. Even though the supersaturation in such systems is so small that it can be neglected in writing a solute mass balance, it is important in setting nucleation and growth rates. In such instances it is convenient to substitute growth rate for supersaturation by combining Eqs. (18) and (25). This gives:

$$B^\circ = k_{\text{nuc}} G^i M_T^j N^k \quad (58)$$

The constant  $k_{\text{nuc}}$  depends on process variables other than supersaturation, magma density, and intensity of mixing; these include temperature and presence of impurities. If sufficient data are available, these variables may be separated from the constant by adding more terms in a power-law correlation.  $k_{\text{nuc}}$  is specific to the operating equipment and not transferable from one equipment scale to another. The system-specific constants  $i$  and  $j$  are obtainable from experimental data and may be used in scale-up, although  $j$  may vary considerably with mixing conditions.

As shown by Eq. (54), growth rate  $G$  can be obtained from the slope of a plot of the log of population density against crystal size; nucleation rate  $B^\circ$  can be obtained from the same data by using the relationship given by Eq. (57), with  $n^\circ$  being the intercept of the population density plot. Nucleation rates obtained by these procedures should be checked by comparison with values obtained from a mass balance (see the later discussion of Eq. (66)).

The perfectly mixed crystallizer of the type described in the preceding discussion is highly constrained. Alteration of the characteristics of crystal size distributions produced by such systems can be accomplished only by modifications of the nucleation and growth kinetics of the system being crystallized. Indeed, examination of Eq. (54) shows that once nucleation and growth kinetics

are fixed, the crystal size distribution is determined in its entirety. In addition, such distributions have the following characteristics:

- Mass density function (from Eq. (39)):

$$m = \rho k_{\text{vol}} n^\circ L^3 \exp\left(-\frac{L}{G\tau}\right) \quad (59)$$

- Dominant crystal size (from Eq. (40)):

$$L_D = 3G\tau \quad (60)$$

- Moments of  $n$  (from Eq. (37)):

$$m_i = i! n^\circ (G\tau)^{i+1} \quad (61)$$

- Total number of crystals per unit volume:

$$N_T = \int_0^\infty n dL = m_0 = n^\circ G\tau \quad (62)$$

- Total length of crystals per unit volume:

$$L_T = \int_0^\infty nL dL = m_1 = n^\circ (G\tau)^2 \quad (63)$$

- Total surface area of crystals per unit volume:

$$A_T = k_{\text{area}} \int_0^\infty nL^2 dL = k_{\text{area}} m_2 = 2k_{\text{area}} n^\circ (G\tau)^3 \quad (64)$$

- Total solids volume per unit volume:

$$V_{\text{TS}} = k_{\text{vol}} \int_0^\infty nL^3 dL = k_{\text{vol}} m_3 = 6k_{\text{vol}} n^\circ (G\tau)^4 \quad (65)$$

- The coefficient of variation of the mass density function (from Eq. (42)) is 50%.
- The magma density  $M_T$  (mass of crystals per unit volume of slurry or liquor) is the product of the crystal density, the volumetric shape factor, and the third moment of the population density function:

$$M_T = 6\rho k_{\text{vol}} n^\circ (G\tau)^4 \quad (66)$$

System conditions often allow for the measurement of magma density, and in such cases it should be used as a constraint in evaluating nucleation and growth kinetics from measured population densities. This approach is especially useful in instances of uncertainty in the determination of population densities from sieving or other particle sizing techniques.

## B. Preferential Removal of Crystals

As indicated above, crystal size distributions produced in a perfectly mixed crystallizer are constrained by the nature of the system. This is because both liquor and solids

have the same residence time distributions, and it is the crystal residence time distribution that gives the population density function the characteristic exponential form in Eq. (54). Nucleation and growth kinetics can influence the population density function, but they cannot alter the form of the functional dependence of  $n$  on  $L$ .

Crystallizers are made more flexible by the introduction of selective removal devices that alter the residence time distributions of materials flowing from the crystallizer. Three removal functions—clear-liquor advance, classified-fines removal, and classified-product removal—and their idealized removal devices will be used here to illustrate how design and operating variables can be manipulated to alter crystal size distributions. Idealized representations of the three classification devices are illustrated in Fig. 17.

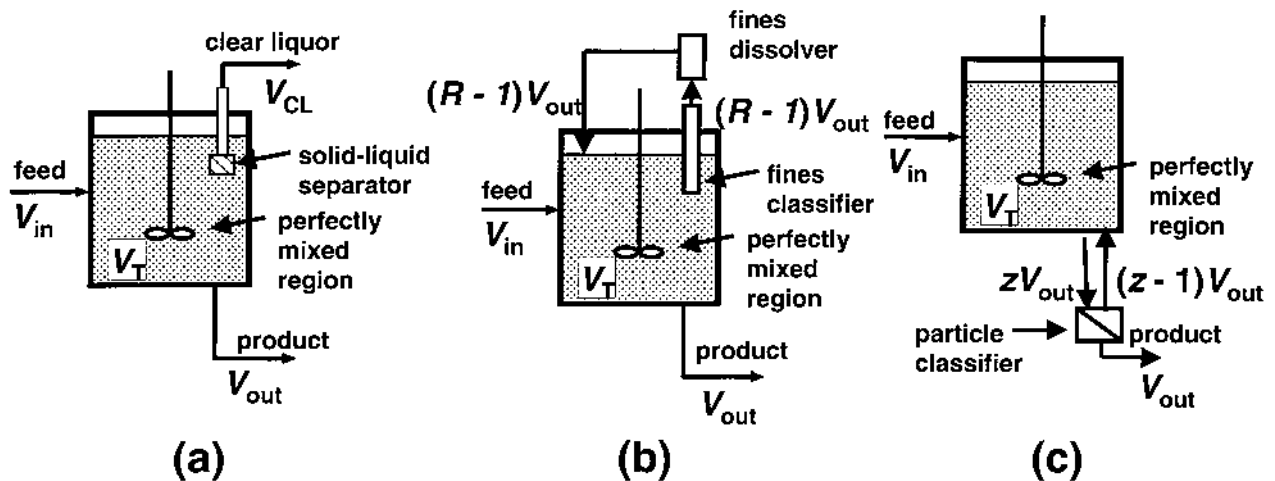
Clear-liquor advance from what is called a *double draw-off crystallizer* is simply the removal of mother liquor without simultaneous removal of crystals. The primary action in classified-fines removal is preferential withdrawal from the crystallizer of crystals of a size below some specified value; this may be coupled with the dissolution of the crystals removed as fines and the return of the resulting solution to the crystallizer. Classified-product removal is carried out to remove preferentially those crystals of a size larger than some specified value. In the following discussion, the effects of each of these selective removal functions on crystal size distributions will be described in terms of the population density function  $n$ . Only the ideal solid-liquid classification devices will be examined. It is convenient in the analyses to define flow rates in terms of clear liquor. Necessarily, then, the population density function is defined on a clear-liquor basis.

Clear-liquor advance is used for two purposes: (1) to reduce the quantity of liquor that must be processed by the solid-liquid separation equipment (e.g., filter or centrifuge) that follows the crystallizer, and (2) to separate the residence time distributions of crystals and liquor. The reduction in liquor flow through the separation equipment can allow the use of smaller equipment for a fixed production rate or increased production through fixed equipment. Separating the residence time distributions of crystals and liquor means that crystals will have an average residence time longer than that of the liquor. This should, in principle, lead to the production of larger crystals, but because the crystallizer is otherwise well mixed, the crystal population density will have the same form as that for the MSMPR crystallizer (Eq. (54)).

The analysis goes as follows: Let  $V_{in}$ ,  $V_{CL}$ , and  $V_{out}$  represent volumetric flow rates of clear liquor fed to the crystallizer, of clear-liquor advance, and of output slurry respectively. The population density function is given by the expression:

$$n = n^{\circ} \exp\left(-\frac{L}{G\tau_{prod}}\right) \quad (67)$$

where  $\tau_{prod} = V_T / V_{out}$ . Increasing  $V_{CL}$  decreases  $V_{out}$  and thereby increases the residence time of the crystals in the crystallizer. Unless the increase in magma density results in significant increases in nucleation, the utilization of clear-liquor advance will produce an increase in the dominant crystal size. Often the increase is much greater than that predicted from theory, and it is suspected that this is because the stream being removed as clear liquor actually contains varying amounts of fines. If this is the case,



**FIGURE 17** Schematic representations of idealized removal functions. (a) Clear-liquor advance, (b) classified-fines removal, (c) classified-product removal.



both clear-liquor advance and fines-removal are enhancing crystal size.

As an idealization of classified-fines removal, assume that two streams are withdrawn from the crystallizer, one corresponding to the product stream and the other a fines-removal stream. Designate the flow rate of the clear solution in the product stream to be  $V_{out}$  and set the flow rate of the clear solution in the fines-removal stream to be  $(R - 1)V_{out}$ . Also, assume that the device used to separate fines from the larger crystals functions so that only crystals below an arbitrary size  $L_F$  are in the fines-removal stream and that all crystals below size  $L_F$  have an equal probability of being withdrawn as fines. Under these conditions, the crystal size distribution is characterized by two mean residence times, one for the fines and the other for crystals larger than  $L_F$ , that are related by the equations:

$$\tau = \frac{V_T}{V_{out}} \quad (\text{for } L > L_F) \quad (68)$$

$$\tau_F = \frac{V_T}{RV_{out}} = \frac{\tau}{R} \quad (\text{for } L \leq L_F) \quad (69)$$

where  $V_T$  is the total volume of clear solution in the crystallizer.

For systems following invariant growth, the crystal population density in each size range will decay exponentially with the inverse of the product of growth rate and residence time. For a continuous distribution, the population densities of the classified fines and the product crystals must be the same at  $L = L_F$ . Accordingly, the population density for a crystallizer operating with classified-fines removal is given by:

$$n = n^\circ \exp\left[-\frac{RL}{G\tau}\right] \quad (\text{for } L \leq L_F) \quad (70)$$

$$n = n^\circ \exp\left[-\frac{(R-1)L_F}{G\tau}\right] \exp\left[-\frac{L}{G\tau}\right] \quad (\text{for } L > L_F) \quad (71)$$

Figure 18 shows how the population density function changes with the addition of classified-fines removal. The lines drawn are for a hypothetical system, but they illustrate qualitatively what can be demonstrated analytically; that is, fines removal increases the dominant crystal size, but it also increases the spread of the distribution.

A simple method for implementation of classified-fines removal is to remove slurry from a settling zone in the crystallizer. The settling zone can be created by constructing a baffle that separates the zone from the well-mixed portion of the vessel—recall, for example, the draft-tube-baffle crystallizer described in Section V—or, in small-

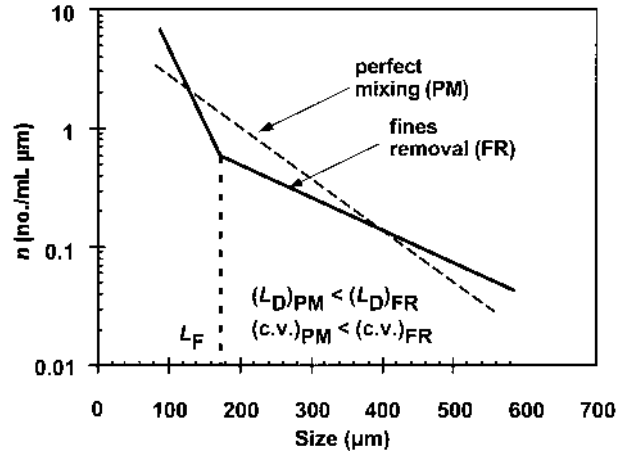


FIGURE 18 Population density plot for product from crystallizer with idealized classified-fines removal.

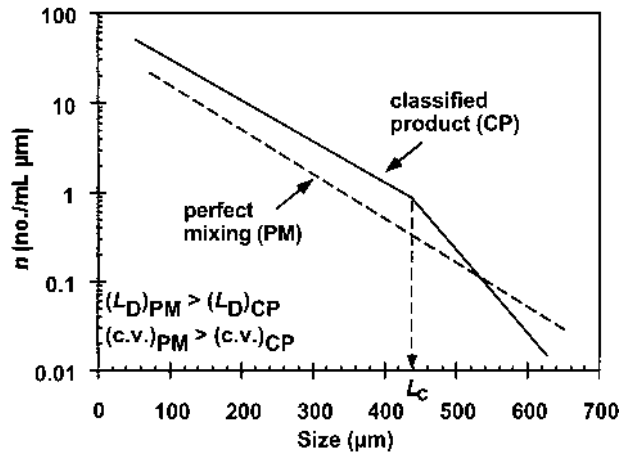
scale systems, by simply inserting a length of pipe or tubing of appropriate diameter into the well-mixed crystallizer chamber. The separation of crystals in the settling zone is based on the dependence of settling velocity on crystal size. Crystals entering the settling zone and having a settling velocity greater than the upward velocity of the slurry remain in the crystallizer. As the cross-sectional area of a settling zone is invariant, the flow rate of slurry through the zone determines the cut-size  $L_F$ , and it also determines the parameter  $R$  used in Eqs. (69) through (71).

In a crystallizer equipped with classified-product removal, crystals above some coarse size  $L_C$  are removed at a rate  $Z$  times the removal rate of smaller crystals. This can be accomplished by using an elutriation leg, a hydrocyclone, or a screen to separate larger crystals for removal from the system. Using the analysis of classified-fines removal as a guide, it can be shown that the crystal population density is given by the equations:

$$n = n^\circ \exp\left[-\frac{L}{G\tau}\right] \quad (\text{for } L \leq L_C) \quad (72)$$

$$n = n^\circ \exp\left[\frac{(Z-1)L_C}{G\tau}\right] \exp\left[-\frac{ZL}{G\tau}\right] \quad (\text{for } L > L_C) \quad (73)$$

where  $\tau$  is defined as the residence time  $V_T/V_{out}$ . Figure 19 shows the effects of classified-product removal on crystal size distribution; the dominant crystal size is reduced and the spread of the distribution becomes narrower. Note that it is impossible for crystals smaller than  $L_C$  to leave the idealized classified-product crystallizer illustrated in Fig. 17c. Accordingly, the population densities shown on Fig. 19 for the classified-product crystallizer represent conditions *inside* the perfectly mixed region of the unit.



**FIGURE 19** Population density plot for crystals in crystallizer with idealized classified-product removal.

If both fines and product are removed on a classified basis, the population density will be given by the equations:

$$n = n^\circ \exp\left[-\frac{RL}{G\tau}\right] \quad (\text{for } L \leq L_F) \quad (74)$$

$$n = n^\circ \exp\left[-\frac{(R-1)L_F}{G\tau}\right] \exp\left[-\frac{L}{G\tau}\right] \quad (\text{for } L_F < L < L_C) \quad (75)$$

$$n = n^\circ \exp\left[-\frac{(R-1)L_F}{G\tau}\right] \exp\left[\frac{(Z-1)L_C}{G\tau}\right] \times \exp\left[-\frac{ZL}{G\tau}\right] \quad (\text{for } L \geq L_C) \quad (76)$$

Selection of a crystallizer that has both classified-fines and classified-product removal is done to combine the best features of each: increased dominant size and narrower distribution. Figure 20 illustrates the effects of both removal functions on population density. Note that this plot of population density results from sampling the magma within a crystallizer, not from sampling the product stream, which for the ideal classification devices considered here can only have crystals larger than  $L_C$ . As discussed earlier for the classified-product crystallizer, the population densities shown in Fig. 20 represent those found in the crystallizer.

The model of the crystallizer and selective removal devices that led to Eqs. (74) through (76) is referred to as the R-Z crystallizer. It is an obvious idealization of actual crystallizers because of the perfect cuts assumed at  $L_F$  and  $L_C$ . However, it is a useful approximation to many systems and it allows qualitative analyses of complex operations.

Although many commercial crystallizers operate with some form of selective crystal removal, such devices can be difficult to operate because of fouling of heat-exchanger

surfaces or blinding of screens. In addition, classified-product removal can lead to cycling of the crystal size distribution. Often such behavior can be minimized or even eliminated by increasing the fines-removal rate.

Moments of the population density function given by Eqs. (74) through (76) can be evaluated in piecewise fashion:

$$m_i = \int_0^{L_F} L^i n dL + \int_{L_F}^{L_C} L^i n dL + \int_{L_C}^{\infty} L^i n dL \quad (77)$$

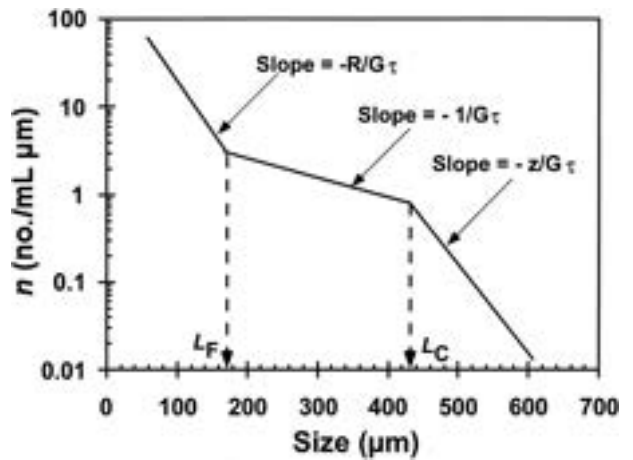
Equation (77) is used to estimate the moments of the population density function within the crystallizer, not of the product distribution. (Recall that moments of the distribution within the crystallizer are often required for kinetic equations.) Assuming perfect classification, moments of the product distribution can be obtained from the expression:

$$m_{i,\text{prod}} = \int_{L_C}^{\infty} L^i n dL \quad (78)$$

Moments can be used to characterize the material produced from or contained in a crystallizer with classified-fines or classified-product removal or to evaluate the effect of these selective removal functions on product characteristics. All that is required is the use of the equations derived earlier to relate special properties, such as coefficient of variation to the operational parameters  $R$  and  $Z$ .

### C. Batch Crystallization

As with continuous crystallizers, the mode by which supersaturation is generated affects the crystal yield and size distribution; however, it is the *rate* at which such supersaturation is generated that is most important in determining product characteristics. Furthermore, there are infinite



**FIGURE 20** Population density plot for crystals in crystallizer with idealized classified-fines and classified-product removal.

possibilities in selecting cooling profiles,  $T(t)$ , or vapor generation profiles,  $V(t)$ , or time dependencies of precipitant or nonsolvent addition rates.

For illustrative purposes, consider that the protocol for a cooling crystallizer can involve either natural cooling—cooling resulting from exposure of the crystallizer contents to a heat sink without intervention of a control system—or manipulation of cooling to reduce the system temperature in a specific manner. In both cases, the instantaneous heat-transfer rate is given by:

$$Q = UA(T - T_{\text{sink}}) \quad (79)$$

where  $U$  is a heat-transfer coefficient,  $A$  is the area available for heat transfer,  $T$  is the temperature of the magma, and  $T_{\text{sink}}$  is the temperature of the cooling fluid. If  $T_{\text{sink}}$  is a constant, the maximum heat-transfer rate and, therefore, the highest rate at which supersaturation is generated are at the beginning of the process. This protocol can lead to excessive primary nucleation and the formation of encrustations on the heat-transfer surfaces.

The objective of programmed cooling is to control the rate at which the magma temperature is reduced so that supersaturation remains constant at some prescribed value, usually below the metastable limit associated with primary nucleation. Typically the batch is cooled slowly at the beginning of the cycle and more rapidly at the end. An analysis that supports this approach is presented later. In size-optimal cooling, the objective is to vary the cooling rate so that the supersaturation in the crystallizer is adjusted to produce an optimal crystal size distribution.

Protocols similar to those described above for cooling crystallizers exist for crystallization modes involving evaporation of solvent and the rate at which a non solvent or a reactant is added to a crystallizer.

A population balance can be used to follow the development of a crystal size distribution in batch crystallizer, but both the mathematics and physical phenomena being modeled are more complex than for continuous systems at steady state. The balance often utilizes the population density defined in terms of the total crystallizer volume, rather than on a specific basis:  $\bar{n} = n V_T$ . Accordingly, the general population balance given by Eq. (51) can be modified for a batch crystallizer to give:

$$\frac{\partial(n V_T)}{\partial t} + \frac{\partial(G n V_T)}{\partial L} = \frac{\partial \bar{n}}{\partial t} + \frac{\partial(G \bar{n})}{\partial L} = 0 \quad (80)$$

The solution to this equation requires both an initial condition ( $\bar{n}$  at  $t = 0$ ) and a boundary condition (usually obtained by assuming that crystals are formed at zero size):

$$\bar{n}(0, t) = \bar{n}^\circ(t) = \frac{B^\circ(t)}{G(0, t)} \quad (81)$$

The identification of an initial condition associated with the crystal size distribution is very difficult. If the system is seeded, the initial condition becomes:

$$\bar{n}(L, 0) = \bar{n}_{\text{seed}}(L) \quad (82)$$

where  $\bar{n}_{\text{seed}}$  is the population density function of the seed crystals. If the system is unseeded, the nuclei often are assumed to form at size zero.

The rate of cooling, or evaporation, or addition of diluent required to maintain specified conditions in a batch crystallizer often can be determined from a population-balance model. Moments of the population density function are used in the development of equations relating the control variable to time. As defined earlier, the moments are

$$m_i = \int_0^\infty L^i \bar{n} dL \quad (83)$$

Recognizing that the zeroth moment is the total number of crystals in the system, it can be shown that:

$$\frac{dm_0}{dt} = \bar{n}^\circ G = B^\circ = \frac{dN_T}{dt} \quad (84)$$

Moment transformation of Eq. (80) leads to the following relationship:

$$\frac{\partial m_j}{\partial t} = j G m_{j-1} \quad (85)$$

Combining Eq. (85) with the relationships of moments to distribution properties developed in Section VI.A for  $j = 1, 2, 3$  gives:

$$\frac{dm_1}{dt} = G m_0 \xrightarrow{m_0=N_T} \frac{dL_T}{dt} = G N_T \quad (86)$$

$$\frac{dm_2}{dt} = 2 G m_1 \xrightarrow{m_1=L_T} \frac{dA_T}{dt} = 2 G k_{\text{area}} L_T \quad (87)$$

$$\frac{dm_3}{dt} = 3 G m_2 \xrightarrow{k_{\text{area}} m_2=A_T} \frac{dM_T}{dt} = 3 G \rho \left( \frac{k_{\text{vol}}}{k_{\text{area}}} \right) A_T \quad (88)$$

where  $N_T$  is the total number of crystals,  $L_T$  is total crystal length,  $A_T$  is total surface area of the crystals, and  $M_T$  is the total mass of crystals in the crystallizer. In addition to a population balance, a solute balance must also be satisfied:

$$\frac{d(V_T C)}{dt} + \frac{dM_T}{dt} = 0 \quad (89)$$

where  $V_T$  is the total volume of the system, and  $C$  is solute concentration in the solution.

The above equations can be applied to any batch crystallization process, regardless of the mode by which supersaturation is generated. For example, suppose a model is needed to guide the operation of a seeded batch crystallizer so that solvent is evaporated at a rate that gives

a constant crystal growth rate  $G$  and no nucleation; in other words, supersaturation is to be held constant and only those crystals added at the beginning of the run are in the crystallizer. Model development proceeds as follows: combining the solute balance, Eq. (89), with Eq. (88),

$$\frac{d(V_T C)}{dt} + \frac{3\rho A_T k_{vol} G}{k_{area}} = 0 \quad (90)$$

Recognizing that the process specification requires  $C$  to be a constant and taking the derivative of Eq. (90):

$$C \frac{d^2 V_T}{dt^2} + 3\rho \left( \frac{k_{vol}}{k_{area}} \right) G \frac{dA_T}{dt} = 0 \quad (91)$$

↓ Eq. (87)

$$C \frac{d^2 V_T}{dt^2} + 6\rho k_{vol} G^2 L_T = 0 \quad (92)$$

Taking the derivative of the last equation:

$$C \frac{d^3 V_T}{dt^3} + 6\rho k_{vol} G^2 \frac{dL_T}{dt} = 0 \quad (93)$$

↓ Eq. (86)

$$C \frac{d^3 V_T}{dt^3} + 6\rho k_{vol} G^3 N_T = 0 \quad (94)$$

Suppose that the batch crystallizer is seeded with a mass of crystals with a uniform size of  $\bar{L}_{seed}$ . The number of seed crystals is  $N_{seed}$ , and, as the operation is to be free from nucleation, the number of crystals in the system remains the same as the number of seed crystals. The initial values of total crystal length, total crystal surface area, total crystal mass, and system volume are

$$L_T(0) = N_{seed} \bar{L}_{seed} \quad (95)$$

$$A_T(0) = k_{area} N_{seed} \bar{L}_{seed}^2 \quad (96)$$

$$M_T(0) = \rho k_{vol} N_{seed} \bar{L}_{seed}^3 \quad (97)$$

$$V_T(0) = V_{T0} \quad (98)$$

On integrating Eq. (94), the following dependence of system volume on time can be obtained:

$$C(V_{T0} - V_T) = k_{vol} \rho N_{seed} [(Gt)^3 + 3(Gt)^2 \bar{L}_{seed} + 3(Gt) \bar{L}_{seed}^2] \quad (99)$$

Therefore, for the specified conditions, the evaporation rate ( $-dV_T/dt$ ) is a parabolic (second-order) function of time, and the rate of heat input to the crystallizer must be controlled to match the conditions called for by Eq. (99).

If a cooling mode is used to generate supersaturation, an analysis similar to that given above can be used to derive

an appropriate dependence of system temperature on time. The result depends upon the relationship of solubility to temperature. If that relationship is linear, the cooling rate varies with time in a parabolic manner; i.e.,

$$-\frac{dT}{dt} = C_1 t^2 + C_2 t + C_3 \quad (100)$$

An approximation to the temperature–time relationship that serves as a good starting point for establishing a fixed protocol is given by:

$$T = T_0 - (T_0 - T_{final}) \left( \frac{t}{\tau} \right)^3 \quad (101)$$

where  $\tau$  is the overall batch run time.

It is clear that stringent control of batch crystallizers is critical to obtaining a desired crystal size distribution. It is also obvious that the development of a strategy for generating supersaturation can be aided by the types of modeling illustrated above. However, the initial conditions in the models were based on properties of seed crystals added to the crystallizer. In operations without seeding, initial conditions are determined from a model of primary nucleation.

## D. Effects of Anomalous Growth

Throughout this section, crystals have been assumed to grow according to the McCabe  $\Delta L$  law. This has simplified the analyses of both continuous and batch crystallizers and, indeed, crystal growth often follows the  $\Delta L$  law. However, as outlined in Section III, size-dependent growth and growth-rate dispersion contribute to deviations from the models developed here. Both of these phenomena lead to similar results: In continuous, perfectly mixed crystallizers, the simple expression for population density given by Eq. (54) is no longer valid. Both size-dependent growth and growth-rate dispersion due to the existence of a random distribution of growth rates among crystals in a magma lead to curvature in plots of  $\ln n$  vs.  $L$ . Models for both causes of this behavior exist but are considered beyond the scope of the present discussion. In batch crystallization, the effects of anomalous growth lead to a broadening of the distribution, as was illustrated in Fig. 6.

## E. Summary

The discussion presented here has focused on the principles associated with formulating a population balance and applying simplifying conditions associated with specific crystallizer configurations. The continuous and batch systems used as examples were idealized so that the principles

could be illustrated, but the concepts can be applied to more complicated configurations. Additionally, there has been a growing body of work on aspects of population balance formulation that greatly extends the ability to describe complex systems. Such work has involved anomalous crystal growth, crystal agglomeration, and crystal breakage and necessarily results in substantially more complex models.

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